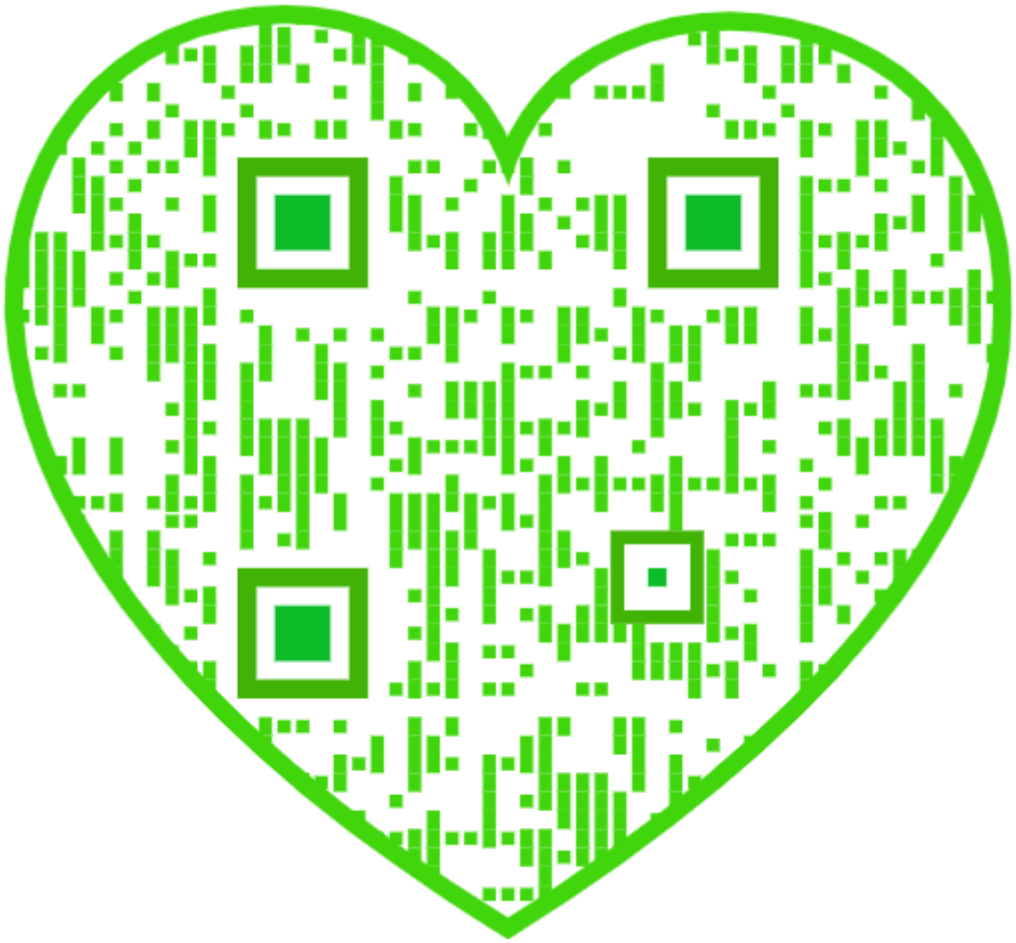

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# APPLIED CHEMISTRY

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## AN ELEMENTARY TEXT BOOK FOR SECONDARY SCHOOLS

BY

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Instructor in Chemistry in Central High School, Kansas City, Mo., for twenty-three years; More Recently Vice-Principal; Author of "Chemistry for Nurses," etc.

*ILLUSTRATED*

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No 1

¶To the hundreds of young men and women, students of mine in the past, whom it has been my privilege to know and to love; especially to my own son, Fredus Nelson, Junior, who in his early childhood, playing at chemistry among the bottles and apparatus of my laboratory, found his chief delight and who now in his early manhood gives promise of attaining to heights in this realm of science of which his father only dreamed, this little book is affectionately dedicated by the author.

# PREFACE

The author is not very sure but that the preface of any book is a useless page. It is doubtful whether a sufficient number ever read this personal letter of the author to pay him for the writing or the publisher for printing it. Yet every writer by force of custom feels compelled to address his readers by a foreword.

Like Livy, in his preface to his History of the Roman People, I do not know whether I am doing a work worth while in putting another text of elementary chemistry before the public; and even if I knew, modesty would forbid that I speak very strongly.

Permit me to say that to me it has never seemed necessary for a high school chemistry to present a mere skeleton of the most interesting of sciences when that skeleton may just as easily be clothed with wonderful symmetry and charming beauty. On the contrary, it has always seemed that a text for secondary schools may and ought to be a readable book just as well as one merely surfeited with facts. No dinner menu is complete which offers nothing but lean meat and vegetables. It may thus contain all that is essential, but far from all that is desired. Entrees and desserts round out the repast and give a sense of satisfaction not otherwise possible.

Such is the attempt of this text, to present the chemical facts of every-day life in a readable form and by so doing make them interesting. If this cannot be done, for most students the book is a failure.

To the teacher let me say that my long experience compels me to believe that very few classes, in a school year of nine or ten months, are able to complete a text of this size.

Some portions must be omitted. No one in a table d'hote dinner is expected to order everything on the bill of fare. Let him use judgment and discretion, the teacher likewise.

Almost a quarter of a century has elapsed since I began my work in Central High School in Kansas City, one of the great high schools of the Middle West. I should not be true to my own better self did I fail to acknowledge my debt of gratitude to the hundreds of students whom I have had in that time. In this particular work I wish to thank especially Mr. J. U. Young, now head of the department of Chemistry of Central High School, Kansas City, for his many valuable suggestions and also Mr. G. W. Davis, of the Northeast High School, Kansas City. I am also under obligations to Mr. G. H. Wilkinson of the Physics Department of Jefferson High School, Los Angeles, Cal., who has been of material assistance in reading the manuscript; to Mr. F. N. Peters, Jr., of the Department of Chemistry of the University of Missouri, for suggestions in methods of presentation of certain gas laws, to Mr. V. W. Peters, of Los Angeles, Cal., for drawings from which many of the illustrations were made; to the Goldschmidt Thermit Co., of New York City, for illustrations of thermit welding, to the Permutit Water Softener Co., of New York, as well as to two or three publishing houses who have extended courtesies in the way of illustrations.

F. N. P.

Los Angeles, California.

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# APPLIED CHEMISTRY

## CHAPTER I

## A STUDY OF MATTER

**Outline—**

- Introduction
- Former Method of Reasoning
- Present Methods of Scientific Investigation
- Old Theories of Matter
  - (*a*) Composition of
  - (*b*) Transmutation
- Present Ideas
- Elements
- Compounds
  - (*a*) Definition of
  - (*b*) Chemical Union
  - (*c*) Method of Naming
  - (*d*) Explanation of Chemical Union
- Chemical Changes
  - Kinds and Illustrations
- Mixtures

1. **Introduction.**—Nearly every normal child is born an interrogation point. Almost as soon as he can form sentences he begins asking "why;" and many a Christmas toy has served best by its sacrifice upon the altar of childish investigation in the effort to learn what makes the noise, or why the wheels go around. The history of the child is largely the history of the human race. Were the spirit of inquiry not crushed out in childhood, grown to youth and maturity, all would still find the greatest pleasure in studying the phenomena of nature. Some few survive the rebuffs and repressions of child-

hood and to them nature ever speaks in loving and fascinating words. Others must have this instinct of investigation revived in their hearts if they find pleasure in any science.

Chemistry as one branch of learning probably enters more largely into the affairs of ordinary everyday life than any other. Without it, not only would most of the great engineering achievements of the world, such as the construction of great bridges and transcontinental railways, and the Panama Canal; not only would the automobile and the airplane and all other modern means of rapid transportation be unknown, but the many little things of life would be mysterious and unintelligible. Cookery is a science dependent in many ways upon chemistry; pure foods and drinks can be kept so only by a knowledge of chemistry; healthful air and sanitary conditions in the home must be secured by a knowledge of chemistry on the part of some one. Careful investigation shows that a knowledge of chemistry must be had for scientific progress in almost every line of human activity. This little book, therefore, will seek to be helpful in furnishing such chemical information as shall be needed in the affairs of the home and in giving added interest to everyday life; such, that these affairs may be administered the more wisely and that nature may speak the more intelligibly; such that those who read may not only add to their own pleasures but contribute to the welfare and happiness of all who may come under their influence.

2. **Source of Scientific Knowledge.**—There was a time in the world's history when scientific knowledge was thought possible of attainment by reasoning alone. Aristotle, it is said, maintained that a vessel filled with ashes or sand would hold as much water as if there were no

ashes or sand in it. He never made the experiment to prove or disprove the truth of his statement and such was the strength of his influence, and such the method of reasoning of the times and long after, that centuries passed before anyone sought to question by experiment the truth of his statement.

3. **Present Methods.**—In this age of the world every statement of scientific fact or supposed fact is submitted to the most rigid and searching examination; not only is reason applied, but every possible method of testing experimentally the truth of the statement is used. To illustrate: Some years ago one of England's greatest chemists announced in a paper read before a scientific gathering that he had succeeded in making a certain amount of lithium from copper by the use of radium. The next morning's sun had hardly risen before many of his hearers were preparing to repeat his experiment, not for the sake of the experiment, but to prove or disprove his claims. So, in the present age of the world, every theory of every scientist, no matter how noted he may be, or however plausible his theory may seem, must be subjected to the test of practical experiment before it can be accepted as a scientific fact.

4. **Some Abandoned Theories.**—As a result of the manner of thought of centuries ago, many theories were accepted as sufficiently plausible which long since have been abandoned. When a vessel of water is left exposed to the air or placed upon some source of heat, the water disappears. Centuries ago it was believed that water upon the addition of heat is changed into air; further, that the air upon the removal of the heat again becomes water. This was based upon a very superficial observation, first the disappearance of the water as stated, and second, its appearance upon the surface of

any cold object brought into a warm room, as upon the outside of a tumbler of ice water. But no careful experiments were ever made to prove or disprove the theory. It was also believed that when water is boiled, a portion of it is converted into an earthy substance. True, upon the inside of the tea-kettle in the kitchen a hard, brittle crust gradually forms, but this is simply mineral matter which has been previously dissolved in the water. Pure water never leaves any such residue. But the old philosophers never made the experiment with pure water, as they might have done, to prove the truth of their position.

5. **Transmutation.**—At the time chemistry had its birth, philosophers believed thoroughly in the possibility of the transmutation of one substance into another. Just as they maintained that water could be changed into earth and air, and air into water, so they believed one metal could be transmuted into another. They had observed some things that to them seemed sufficient evidence. Often, in their copper mines they had noticed that the iron tools left standing for some time in the water, which seeped in, became reddish in color and looked as if the iron were changing to copper. This may be seen by putting a bright nail or knife blade into a solution of blue vitriol for a minute or two. A deposit of copper really forms upon the iron, but it may be shown experimentally that the two metals are simply being exchanged for one another and that the iron is not changing into copper. They knew also a process for making brass by fusing copper with an ore of zinc which they called *cadmeia*. They recognized there were vast differences between brass and gold, yet never did they doubt that it was entirely pos-

sible to change iron into copper and this into gold; in fact they strongly believed in the possibility of transmuting any metal into any other if they could but learn the method.

6. **Matter.**—Matter is anything which occupies space, and may be visible or otherwise. Thus, air is matter just as much as is water or wood or iron. What the real composition of matter is has long been one of the great questions of man. There have possibly always been those who believed that there is but one kind of matter in all the world, and that everything we know is simply a modified form of this one kind. On the basis of such a theory it was not hard to believe in the transmutation of the metals. Others claimed there were four primary substances,—earth, air, fire, and water, and that these in a way could be changed from the one into the other.

7. **Present Theory.**—Robert Boyle, sometimes called the Father of Physics and Chemistry, who was born in 1626, advanced the theory that there is a large number of kinds of matter, how many no one knows. To these primary forms he gave the name of *elements,* and the truth of his view has long been accepted by most of the scientific world. According to this idea, an element is a substance that cannot be divided into two or more kinds of matter. Thus gold is believed to contain only gold and copper nothing but copper. At present there are known 83 elements, the greater portion of which exist in comparatively small quantities, and most of which have been discovered since the beginning of the nineteenth century. Of these, eleven are gases, two are liquids, and the others solids. Some of the rarer may on more careful study be found not to be elements, while others as yet unknown will probably be

discovered. It is estimated that two elements, oxygen and silicon, constitute about 75 per cent of all the matter of the earth and seven others nearly all the remaining 25 per cent. Clark gives this table:

| | Per cent |
|---|---|
| Oxygen | 49.98 |
| Silicon | 25.30 |
| Aluminum | 7.26 |
| Iron | 5.08 |
| Calcium | 3.51 |
| Magnesium | 2.50 |
| Sodium | 2.28 |
| Potassium | 2.23 |
| Hydrogen | 0.94 |

The same facts are shown more graphically in Fig. 1.

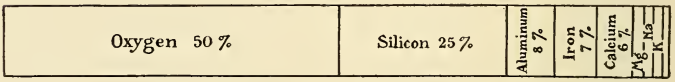



Fig. 1.—Abundance of certain elements.

8. **Compounds.**—A compound is a substance containing two or more elements chemically united and invariably in the same proportion by weight. The most familiar of all compounds is water, which consists of two elements, hydrogen and oxygen, always in the proportion of 1 to 8. Common salt is another compound containing the two elements, sodium and chlorine, always united in the proportion approximately of 46 to 71.

9. **Chemical Union Defined.**—In defining a compound in the preceding paragraph the expression, chemically united, was used. If two substances are mixed, the resulting product will partake of the nature of each ingredient. Two white substances will give a white product, a red and white will give a pink, a white and black

a gray. But if two substances differing from each other unite chemically the product formed may not partake of the properties of either even to the slightest extent, and will be essentially different. To illustrate: Hydrogen and oxygen are both colorless gases, the former inflammable; the latter essential for life and ordinary combustion. When the two unite chemically, at ordinary temperatures, the resulting product is a liquid, which is not only not inflammable but will even extinguish fire and cannot be inhaled. Sodium, in common salt, is a soft metal, silvery white in color, which upon the moistened hand or in the mouth would catch fire and produce most serious burns. Chlorine, the other ingredient, is a heavy yellow gas, terribly destructive of life if inhaled and used with frightful results in the late great war. When these two unite chemically each loses its properties, and the two produce an entirely new substance, not only not harmful, in ordinary quantities, but even regarded as an essential in the animal economy. Likewise, two white substances, uniting chemically, may produce a brilliant red, as do potassium iodide and mercuric chloride; two gases may form a solid, as will ammonia and hydrogen chloride; two liquids a solid. Many of these in great variety will be taken up from time to time and need not be emphasized here.

10. **General Plan of Naming Compounds.**—A few general statements as to how compounds are named will be helpful at this time. In the early days of chemistry no plan was followed in naming the various substances prepared. As a result, peculiar and fantastic names of very familiar things have come down to us. At the present time so vast is the number of compounds known —hundreds of thousands—that some very definite and systematic method is necessary. In most cases as soon

as a chemist hears the name of a compound, he knows its composition even though it may be one not familiar to him. Common salt is chemically known as sodium chloride, and one knows immediately that it consists of sodium and chlorine; if the name ends in *ide* the compound contains only the elements mentioned, which, except in a few cases, are but two in number. Thus, mercuric chloride contains mercury and chlorine; potassium iodide, potassium and iodine. If the name of the compound ends in *ate*, with few exceptions which need not be mentioned here, the compound contains oxygen, in addition to the other elements named. Thus, sodium chlo-

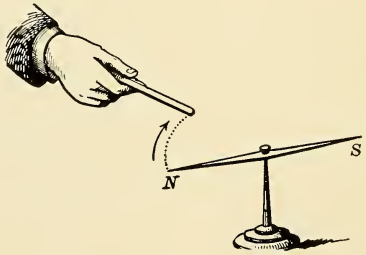



Fig. 2.—Showing the "north" end of a magnetic needle being attracted by the "south" end of another.

rate contains sodium, chlorine and oxygen; potassium sulphate, potassium, sulphur and oxygen.

11. **What Elements will Unite?**—Not every element will unite with every other element. If two magnets, either bar or horseshoe, be placed together, end to end, there will be no attraction if the two ends marked — are brought together or likewise if the two marked +; but if an end marked + be brought up to one with the opposite sign they adhere strongly. This is always true. Everyone is familiar with the ordinary compass, often spoken of as the mariner's compass. If the end of the

needle which points north be approached by the north end of a similar magnetic needle, the one free to move will swing away; if the opposite end be approached they will attract each other. (See Fig. 2.) From these facts a simple law has been formulated: "Like poles repel and unlike poles attract each other." If the ends of two wires connected with an electric battery be dipped in a solution through which the current can pass in a U-shaped tube as shown in Fig. 3, the wire upon which the current enters is spoken of as the *anode,* from a Greek word meaning the *road in* and the wire upon which the current passes out is called the *cathode,* or the *road out.* Often the

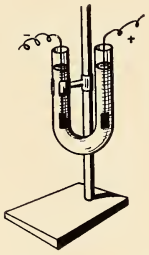



Fig. 3.—The wire marked + is the anode and the other is the cathode.

anode is called the positive and the cathode the negative electrode. Now if the solution used be one of common salt, sodium chloride, it will be found that the sodium always collects at the cathode and the chlorine at the anode. For this reason, applying the law stated above, sodium is regarded as a positive element and chlorine as a negative. In general, in all similar compounds the metal collects at the cathode and the other element at the anode. Hence, all such consist of a positive and a negative element or group of elements. In naming such compounds the positive is always given first. Thus, sodium chloride contains a positive element, sodium, and a negative ele-

ment, chlorine. Copper sulphate contains copper, a positive element and a negative group, consisting of sulphur and oxygen. It would seem then from these statements that chemical union is a kind of electrical attraction.

12. **Chemical Changes, Kinds.**—There are several kinds of chemical changes; in all cases the identity and the characteristics of the substances involved are lost or destroyed. This has been illustrated in the case of hydrogen and oxygen uniting to form water and of sodium and chlorine, to form common salt. Such as these are very simple and are known as *"Additive Reactions,"* an expression which indicates that the two substances have been *added* or *joined together* and have formed a single substance. Another similar and very familiar case is that of flashlight powders used in photography. The essential ingredient, that which produces the intensely white light, is magnesium, a steel-gray metal which has been powdered. In burning, it simply combines with oxygen, producing a white compound known as magnesium oxide, often called magnesia, used in cleaning felt hats, kid gloves, as a dressing for white shoes and for similar well-known purposes.

13. **Simple Decomposition.**—Another kind of chemical change equally simple as the preceding is known as *"Simple Decomposition."* In such changes the process is the reverse of the additive. A single compound by heat or some other force is decomposed into its component elements. To illustrate by a familiar example, mercuric oxide, a compound whose name indicates its composition, if heated strongly is decomposed into mercury, which collects upon the sides of the vessel in which it is heated, and oxygen, which is invisible, but which may be detected by holding a pine splinter with a spark upon the end above in the outgoing current of gas. The splinter will

burst into a flame. Likewise, if a current of electricity be passed through water acidulated to render it a conductor, it will decompose the liquid into the two gases of which it is composed.

14. **Metathesis, or Double Decomposition.**—By far the greater number of chemical changes are not as simple as the two kinds already mentioned. More frequently two, and sometimes more than two, substances unite or *react* with each other, in which case both substances are decomposed and two or more new ones are produced, by a rearrangement of the elements contained in the compounds. Such a change is spoken of as *"Metathesis"* or *"Double Decomposition."* It may be illustrated by adding a few cubic centimeters of a solution of potassium iodide to one of mercuric chloride in a test tube. Two new substances are formed, both entirely different from the original, one of them now a brilliant red color and not soluble in water. Numerous illustrations of this kind of change will be had from time to time. Really, metathesis is but a combination of the other two kinds of change in which both or all of the substances used are decomposed and the products combined in a new way.

15. **Mixtures.**—A mixture differs from a compound in that the composing substances do not *unite* with each other as in additive reactions; neither is there any *rearranging* of the elements into new groupings. Further, as a rule, no definite amounts of the two substances are used, or at least are not necessary. The particles of one intermingle with those of the other, but each retains all its own properties. White sand may be mixed with common salt, but neither has lost its distinguishing properties. A little placed on the tongue will possess a salty taste and at the same time will have the gritty feeling of the sand. Moreover, one may readily be separated from the other

by adding water, stirring and after a few minutes decanting or filtering. A common case given by nearly all books is that of fine iron filings and flowers of sulphur. Mixed together, the result is a greenish-gray powder, but neither has lost its distinguishing properties, and as in the case of the salt and sand they may be readily separated. With patience most of the iron filings may be successfully separated from the sulphur by a good magnet. An easier and more satisfactory method is to add carbon disulphide which upon shaking will dissolve the sulphur as water will salt. The dissolved sulphur may then be poured off through a filter paper; if the filings are washed with another portion of the carbon disulphide all the sulphur may be removed. By evaporating the liquid the sulphur may be recovered with all the properties it possessed before. If, however, the intimate mixture be heated for some time strongly in a test tube, the resulting mass will be black instead of greenish, will not be attracted by the magnet as the filings were, and the sulphur cannot be removed by solution. Chemical union has taken place and we now have a compound of iron and sulphur, called iron sulphide.

### Exercises for Review

1. Do you believe Aristotle's statement about the globe of sand? Give reason for your answer.

2. At the present time how is scientific truth obtained? Can reason aid at all in the discovery of Nature's laws? Explain.

3. What was the old idea regarding the relation of water to air? What facts had they to cause such a belief?

4. What is meant by transmutation? What led the ancient philosophers to believe in such a thing? Do you believe it possible? Why?

5. What is matter? How many kinds can you find in this book? In this room? Give two old theories about the composition of matter.

6. What was Boyle's idea of matter? What is the present idea? Is this necessarily the true idea? Explain.

7. Define an element. How many are known? How many are liquids? Solids? How many constitute nearly the whole of the earth? What two are the most abundant?

8. What is a compound? Name two and give composition. Explain what is meant by chemical union. Illustrate.

9. What is the general plan of naming compounds? Give the signification of the endings *ide* and *ate*. Give illustrations.

10. Into what two classes are elements divided? Will copper and silver unite to form a compound? Give reason for your answer.

11. How can one learn experimentally whether an element belongs to one class or the other? Give meaning of the terms *anode* and *cathode*. What synonyms are sometimes used?

12. Name three kinds of chemical changes. Give illustration of each. Show how the third may be regarded as a combination of the other two.

13. How does a mixture differ from a compound? Name two mixtures and give some easy way of separating them.

# CHAPTER II

## WATER AND HYDROGEN PEROXIDE

**Outline—**

Forms of Appearance
Characteristics of Pure Water
Water in the Human Body and Foods
Necessity of Water to the Body
Proof of Composition
    (*a*) By Electrolysis
    (*b*) By Weight
Law of Definite Proportions
Water of Combination
    Hydrates
Efflorescence
Deliquescence
Domestic Water Supplies
City Water Supplies
Hydrogen Peroxide
Law of Multiple Proportions

1. **Its Familiarity.**—Water is at once the most familiar of all natural substances and one of the most interesting. It appears in a very large variety of forms, all more or less familiar: in partially condensed vapor as fog; in the feathery *cirrus* cloud; the billowy *cumulus*, the beautiful summer cloud; the stormy and threatening *nimbus*. In the solid form as snow, hail, ice, glaciers and icebergs.

2. **Characteristics of Water.**—Pure water is tasteless, odorless and colorless, except in great depths as lakes and seas, when it appears blue or bluish green. It is often said that distilled water tastes flat, but this is because we are accustomed to drinking water somewhat impure. Just as beans or potatoes or other vegetables served without salt would taste flat so does water with-

out the usual impurities. Pure water when evaporated leaves no residue, hence would form no incrustation on the inside of kettles or boilers.

3. **Water in the Human Body.**—Not only does water appear in such variety of form and such quantities in nature, but it constitutes a very large proportion of the animal body. Only about 40 per cent of the human body is solid matter, while in the lower animals the percentage of water is much higher. Our foods are also high in water content. Even butter and flour, which we often think of as dry, contain as much as 12 to 14 per cent of water for the former, and 10 to 11 for the latter. The following table will give an idea as to many of the common food products:

TABLE

| | Per cent |
|---|---|
| Beans, dry | 12.60 |
| Beans, string | 89.00 |
| Bread, yeast | 36.12-37.70 |
| Cabbage | 91.50 |
| Carrots | 88.20 |
| Cauliflower | 92.30 |
| Celery | 94.50 |
| Cheese | 34.38-38.60 |
| Corn, dry | 13.12 |
| Eggs | 73.67 |
| Flour, wheat | 10.11 |
| Meat, lean beef | 67.00-70.00 |
| Meat, lean pork | 60.00 |
| Meat, veal | 73.30 |
| Mutton | 50.20 |
| Oat Meal | 12.37 |
| Peas, dry | 12.62 |
| Peas, green | 79.93 |
| Potatoes, sweet | 75.00 |
| Potatoes, white | 66.10-80.60 |
| Rice | 13.11 |
| Turnips | 89.60 |
| Watermelons | 92.40 |

4. **Value of Water to Animals and Plants.**—Nothing need be said about the value of water in the household. Life itself is impossible without it, to say nothing of the comfort it brings. Digestion is merely a process by which solid foods are made soluble that they may be carried through the blood to all parts of the body. As water is the most nearly universal solvent it enters largely into the process of digestion. Assimilation of food is impossible in the absence of water; and not only is this true, but most of the waste matter of the body is carried away dissolved in water or mixed with it in large amounts. On account of its high *specific heat,* that is, a given amount of water contains more heat energy than the same weight of any other liquid at the same temperature, it is regarded as the best means of warming houses in severe weather. It is this very fact that tempers the winters in the Great Lake regions and along the oceans, and renders the climate of countries washed by the Gulf Stream and Japan Current far warmer than other countries in the same latitude not thus favored. In the human body, the blood, largely water, in constant circulation, tends to keep the body of perfectly uniform temperature. In summer, the body is cooled by the rapid evaporation of the water in the blood through the pores of the skin; thus, summer and winter, the water in the body serves to keep a uniform temperature throughout. To maintain the supply thus needed, an ordinary person requires from two to three pints of water per day, in summer more than in cold weather. Plants, likewise, must have water to enable them to absorb the necessary substances of food value from the soil, as also, to make the cellulose, starch and sugar, which they store up in their stems, seeds and fruits.

5. **Composition of Water.**—By volume, water is composed of hydrogen, two parts, and oxygen, one part. This is usually shown experimentally by the Hoffman apparatus (Fig. 4). R is a reservoir into which the water is poured in filling the apparatus. It is necessary to use water slightly acidulated with some acid, as sulphuric, since pure water is not a conductor of electricity. In filling the side tubes, B, B, the stop-cocks are carefully opened, one at a time, and the water allowed to flow in until it barely reaches the stop-cock level.

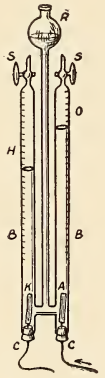



Fig. 4.—Electrolysis or Hoffmann apparatus.

Not much more should be put into R than will fill the three tubes, for a small amount of water makes a large quantity of gas and this forces the excess back into the reservoir, hence room must be left to receive it. Platinum strips, A, A, serve as electrodes and are connected with the source of current by means of wires sealed in glass tubes passed through the corks, C, C. When everything is ready the current is turned on; bubbles immediately begin to rise from both electrodes, much faster from the cathode than the anode. After a few moments

the quantity of gas in each tube may be read from the graduations etched on the tubes, B, B. It will be found that the quantity of one gas is always double that of the other. To know that the smaller volume is oxygen, hold a splinter with a spark on the end over the tip of the tube and carefully open the stopcock. The pressure of the water in R will force the gas out and ignite the splinter. This characteristic test for oxygen has been mentioned in the preceding chapter. The usual method of testing hydrogen is by lighting it. A burning match or better, a small candle, brought to the tip of the tube containing the larger quantity of gas, will ignite it when the stop cock is cautiously opened. The flame at first will be invisible, or until the glass becomes red-hot; but a piece of paper held to it will be instantly ignited, thus showing the presence of a flame.

6. **Explanation of the Experiment.**—Students frequently ask why the hydrogen goes to the cathode or negative electrode, and the oxygen to the anode. This will be readily understood if it is remembered what was said in the preceding chapter about compounds consisting of a positive and a negative element or group. Since oxygen belongs to what we call the negative group, it would necessarily be attracted to the anode: while hydrogen, being positive, would be attracted to the negative electrode.

7. **Proof of Composition by Weight.**—Since gases are very light substances it is necessary to obtain their weights indirectly in this experiment. In Fig. 5 hydrogen is obtained from any suitable generator, K, which for convenience may well be a Kipp apparatus. In order that the gas may be perfectly dry it is allowed to bubble slowly through a wash bottle, containing concentrated sulphuric acid, which is an excellent dry-

ing agent in that it absorbs water readily. The tube, T, made of hard glass, contains copper oxide, preferably in what is known as the wire form. Before connecting, this tube with contents is carefully weighed. In the U-tube calcium chloride in small lumps is placed, the tube and contents carefully weighed and connected to the combustion tube as shown. The hydrogen is then turned on, the heat applied, gently at first, until the glass is well warmed, and the operation continued until the contents of C have become red like bright copper. The heat is then turned off, the hydrogen allowed to flow until the tube is cooled enough to handle comfort-

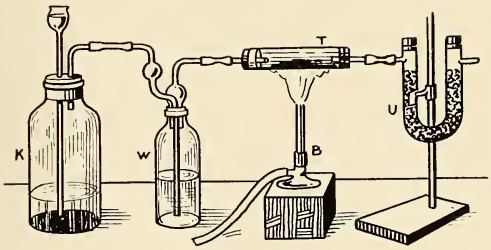



Fig. 5.—Composition of water by weight.

ably when both T and U with contents are again carefully weighed. What has happened is as follows: Hydrogen has the power of taking oxygen away from many oxides when heated strongly. It does so in this case and leaves in the combustion tube mostly pure copper. The loss of weight in this tube, therefore, is the weight of the oxygen used. The hydrogen and oxygen at the temperature present combine to form water, which in the condition of vapor passes over and is absorbed by the calcium chloride in tube U. The gain here, therefore, is the weight of the water produced. Subtracting the weight of the oxygen used from that of the water formed

gives the weight of the hydrogen. Allowing for experimental errors which are always possible, it will be found that the average of a large number of experiments carried out thus is always 8 parts of oxygen to 1 of hydrogen. A typical case with data obtained by actual experiment is given below:

| | |
|---|---|
| Copper oxide and tube before heating | 37.23 grams |
| Weight of same, after heating | 29.87 |
| Loss, which is oxygen | 7.36 |
| Calcium chloride and tube, before heating | 25.18 |
| Weight of same, after heating | 33.46 |
| Gain, which is the water | 8.28 |
| Subtracting the oxygen from weight of water | 0.92 |
| Ratio of oxygen, 7.36, to hydrogen, .92, is 8 to 1 | |

8. **Law of Definite Proportions.**—It was stated in the preceding chapter that a compound is a substance containing two or more elements united in a fixed and definite proportion by weight. The above experiment illustrates the definition and at the same time shows proof. Out of this truth, which applies to all compounds, grows the "Law of Definite Proportions," which is usually stated thus: *When two or more elements unite chemically to form a compound they always do so in the same fixed and definite proportion by weight.* Why they must necessarily do this will be taken up at another time in Chapter VI.

9. **Hydrates—Water of Combination.**—All have seen various substances in crystalline form, such as rock candy, alum, blue vitriol, or such natural compounds as iron pyrite, silica, called rock crystal, and galena. Crystals of artificial compounds are usually prepared by dissolving the substance in water and allowing the water to evaporate. When this occurs, very often a considerable portion of the water combines with the dissolved

solid instead of passing off into the air. Sometimes the water thus combined weighs even more than the solid itself. The water thus taken up is called *water of combination* or sometimes water of crystallization, and the compound thus formed is called a *hydrate*. Familiar examples of hydrates are blue vitriol, Epsom salts, alum, sal soda, and green vitriol.

TABLE SHOWING A FEW HYDRATES AND AMOUNT OF WATER

| | |
|---|---|
| Alum, common | 45.57 per cent |
| Blue Vitriol | 36.14 |
| Borax | 47.12 |
| Epsom salts | 51.22 per cent |
| Green Vitriol | 45.32 |
| Sal Soda | 62.93 |

10. **Efflorescence.**—Hydrates may be regarded as true compounds, for they differ greatly in their physical properties from the *anhydrous* compound. Thus, ordinary hydrated copper sulphate is deep blue in color, and occurs in more or less regularly-shaped triclinic crystals. Anhydrous copper sulphate is white in color and when crystalline, which is not common, is in slender needle-like crystals. However, this combination is rather an unstable one. By heat, usually the water of the hydrate may be removed without affecting the composition of the remaining portion of the compound at all. Even at ordinary room temperatures in many cases considerable portions or all of the water of combination spontaneously passes off into the air. The extent of this loss depends upon the humidity of the air, the temperature and the *specific* rate of the particular compound itself. This may be seen in an interesting little experiment. A manometer as shown in Fig. 6 is attached to a side-neck test tube. A bent glass tube may serve as a manometer if no other is at hand. A rubber cork

is fitted snugly into the test tube filled about half full of mercury. The bent tube also contains mercury at the same level in both arms. A crystal of some hydrate, such as sodium sulphate is put upon the mercury in the test tube and the cork carefully inserted again so as not to disturb the level of the mercury in the bent tube, M. Even at the room temperature water will escape from the crystal, producing pressure upon the mercury in the manometer, moving it up the longer arm, until there is

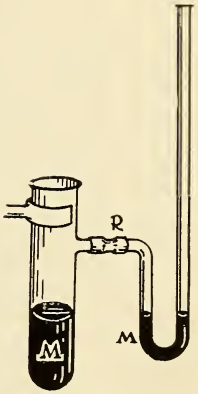



Fig. 6.—Manometer, used in testing gas pressure.

equilibrium. At this point no more water escapes from the hydrate on account of the pressure exerted upon it. Now, if the temperature be raised a few degrees, more water will be expelled and the mercury will rise in the outer arm still higher, until the added pressure again equals the vapor pressure of the water in the crystal. Upon cooling the equilibrium is again disturbed and through the pressure of the mercury the hydrate will absorb water vapor until there is again equal pressure within and without the hydrate. In the open air, as the pressure is not increased by the escape of the water, the loss

continues until no more can be driven off at that temperature. A considerable number of hydrates are able to part with all their water at ordinary room temperature and usual atmospheric conditions. Such hydrates are said to be *efflorescent*. Efflorescence may be defined as the property which some hydrates possess of giving off to the air their water of combination and of crumbling to a powder. The word, literally translated, means *becoming flowers* or *flour*, that is, a fine powder. When efflorescence occurs, the crystalline structure of the substance is destroyed and usually a powder results. Such hydrates as sal soda, often called washing soda, ferrous sulphate, and Glauber's salt, or sodium sulphate, are excellent examples of efflorescent hydrates.

11. **Deliquescence.**—Deliquescence may be defined as the property some substances have of attracting moisture from the air in such quantities as to be dissolved in it. The word means *becoming liquid*. Two such substances have been mentioned already, used in the experiment for the determination of the composition of water by weight, sulphuric acid and calcium chloride. They have frequent applications in the chemical laboratory for drying gases. As calcium chloride is a by-product of certain industries and very cheap, it has been tried by the United States government experimentally as a preventive of dust on roadways, instead of frequent sprinkling. Obviously it could not be used thus where there is much rain in the summer season, since, on account of its great solubility, it would be quickly washed away. Other good examples of deliquescent substances are caustic soda, often called lye, and caustic potash. A *hygroscopic* substance is one that will in damp weather absorb moisture from the air in sufficient quantities to become moist but not to liquefy. For example, common salt in our homes

often becomes damp in rainy weather but it never liquefies, hence is hygroscopic rather than deliquescent. Really, however, in this case the condition is due to the presence of a small quantity of a deliquescent substance, such as magnesium chloride, and not to the salt itself being hygroscopic.

12. **Domestic Water Supplies.**—Water is the most nearly universal solvent known. Glass, rocks and minerals of all sorts, which ordinarily are thought of as insoluble in water, when left for long periods in contact with water, do dissolve appreciably. This is the source of all mineral and hard waters. Organic impurities likewise and substances of all sorts are dissolved by water, so that especially in towns and cities, but in reality everywhere, the domestic supply of water must be carefully guarded. Cisterns, springs and wells in large towns and cities are never safe, and frequently not in smaller places. Sewage and seepage from cess pools make their way through the soil to all such sources of water and cause serious contamination. The water may be perfectly clear and tasteless, yet absolutely unfit to drink. Only chemical and bacteriologic tests can show and in case of doubt these should be applied.

13. **Rivers as a Source of Supply.**—Probably more of the large American cities obtain their water supplies from rivers than from any other source. It would seem at first thought that such would be open to the greatest objection, because of the fact that they are the common means used by cities in disposing of their sewage, and are accessible to contamination in various ways. Fortunately, however, nature has a method of destroying such impurities. Exposure to the air in a flowing stream, especially if the bed be rocky so as to cause an

agitation of the water and to bring all portions of it to the surface, soon results in the destruction of most organic impurities. The city of Los Angeles obtains its water supply from the Owens River, bringing it over two hundred miles. When it enters the upper end of the San Fernando valley it dashes rapidly down in an open viaduct over a very rocky artificial bed, such that the water is churned into a foam, thoroughly impregnating it with air. A very noted case was brought to the attention of the public a few years ago when St. Louis brought suit in the courts against Chicago on the grounds that the latter city was contaminating the water supply of the former by conveying vast quantities of sewage through the Illinois River into the Mississippi not far above the intake of the St. Louis supply. Numerous analyses of the water were made, but bacteriologic and chemical tests failed to sustain St. Louis in her claims. Nevertheless, pathologic bacteria are able to withstand long exposure of this character and daily tests of city water must be made. If the water be muddy, as it may be more or less all the time, and very much so at certain seasons, further purification is necessary. Briefly stated, the steps are about as follows: The river water is pumped into huge basins or reservoirs, where a stream of lime water and another of a solution of alum or some other coagulant, are allowed to enter through pipes. These two solutions in meeting produce a coagulum or gelatinous precipitate which in settling carries practically all the mud with it. Naturally, as most of the bacteria present are attached to mud particles, they are carried down also. At intervals this accumulated deposit is washed back into the river. In very large cities, such treatment is usually supplemented by filtration basins from which the water passes out through thick layers

of sand and gravel as is shown in Fig. 7. Finally, before the water begins its journey to the mains of the city, either liquid chlorine or a solution of bleaching powder in small quantities is introduced for the purpose of destroying any pathologic bacteria which may remain.

14. **Lakes as a Source of Supply.**—Many cities obtain their supply from lakes either natural or artificial. In such cases, unless the lake be large such as those upon which Chicago, Cleveland and other northern cities are located, another serious problem is confronted. A cer-

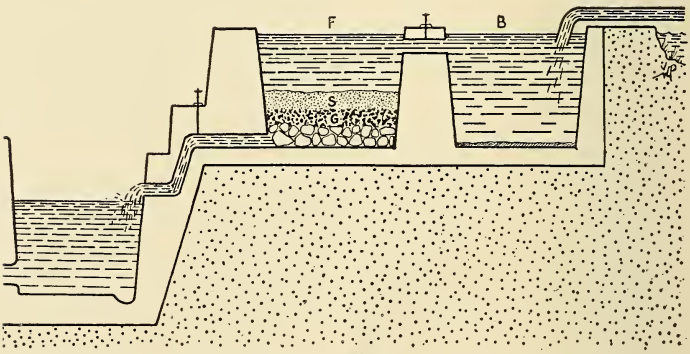



Fig. 7.—Diagrammatic view of city water plant. *B*, the settling basin; *F*, the filter, in the bottom of which are layers of sand and gravel, indicated by the letters *S* and *G*.

tain kind of algæ, a species of plant to which the common green scum seen upon stagnant ponds belongs, grows in the water and late in summer produces spores which upon bursting liberate a very offensive odor, so that the water cannot be used for drinking or cooking. It has been found that the presence of a minute quantity of some copper compound, as blue vitriol, will prevent the growth of such algæ. Accordingly, a burlap sack, filled with blue vitriol crystals, is suspended from a

boat and is rowed back and forth across the lake in every direction for hours or days, until the copper compound is dissolved. The amount of blue vitriol present is so small as to have no appreciable effect upon the human system, but is destructive to the algæ. By some it is thought that the copper enters into combination with the albumin of the algæ and settles to the bottom. If this be the explanation, then there is none left in the

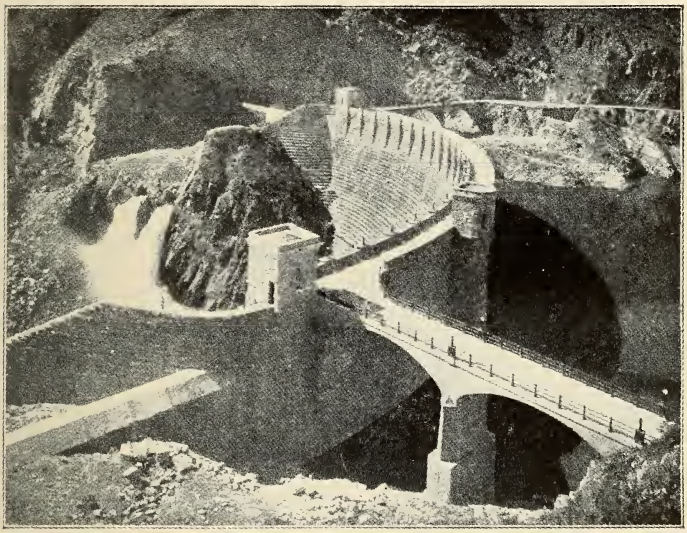


Fig. 8.—Roosevelt Dam, which is very similar to the one at Sweetwater.

water. There are several cities of the southern states which have had to adopt this plan; but one of the most noted is that of Sweetwater Dam a few miles from National City and San Diego in southern California. It is a huge reservoir in a mountain valley, formed by a concrete dam and holds at its capacity several billion gallons of water. See Fig. 8, a typical dam for such water systems.

## HYDROGEN PEROXIDE

15. **Composition.**—In composition, hydrogen peroxide, or dioxide, as it is often called, closely resembles water. Instead of having eight parts of oxygen to one of hydrogen, as is the case with water, it has sixteen of oxygen to one of hydrogen. This added amount, however, is held very loosely, much as is true of the water contained by many hydrates. As a result, therefore, it is escaping at all times, unless in tightly corked bottles, which should be kept in a cool place. Even then the oxygen escapes until sufficient pressure is attained in the bottle to produce equilibrium between the vapor tending to escape from combination and that of the air above. This explains why the cork comes out with a "pop" when it has not been previously removed for some time. Hydrogen peroxide is put on the market in the form of a weak solution, usually about 3 per cent, not only under the name of hydrogen dioxide but also as *dioxygen*.

16. **Uses.**—The value of dioxygen as an antiseptic depends upon the oxygen being continually liberated. Just as flowing water is purified by the oxygen of the air, so bacteria in wounds and diseased portions of the body are destroyed by this more concentrated or more active oxygen. It will be observed that when this additional amount of oxygen is removed from the dioxide, only water remains, which cannot cause irritation. Hence, hydrogen peroxide is probably the safest as well as one of the most efficient germicides for general use. It is also a good bleaching agent and is employed successfully for silks, wool, ivory, feathers and hair, animal products which would be seriously injured by more powerful agents such as chlorine.

17. **Method of Testing.**—The usual method of testing a solution of hydrogen peroxide is by adding a few drops of it to some starch mucilage or very thin paste to which has previously been added a very small quantity of potassium iodide solution. A deep blue solution results. Another sensitive test is to add some potassium dichromate solution to one of hydrogen peroxide acidulated slightly with sulphuric acid. A deep blue color forms which lasts but a moment. It is not known what this blue substance is, because its temporary character prevents any examination of it. If some ether be added before putting the peroxide into the dichromate the deep blue compound is more permanent; by shaking, the ether layer may be made to take up most of the color, so that the test is thus intensified.

18. **Law of Multiple Proportions.**—It has been seen that the composition of water is oxygen, eight parts, hydrogen one; hydrogen peroxide, oxygen, sixteen, hydrogen one. Thus two elements, uniting in different proportions, form two different compounds. In doing so, for a certain fixed amount of hydrogen the oxygen is twice as much in one case as the other, that is, it varies in a simple ratio. This has been found to be generally true and in chemical union for a fixed amount of one element, the other will always unite in some simple ratio as 1:2, 1:3, and the like. Dalton formulated this in what is known as the "Law of Multiple Proportions." Briefly stated it is, *When two or more substances unite in different proportions to produce two or more different compounds, for a fixed amount of one, the varying quantities of the other will always bear some simple ratio to each other.* Later, reasons will be seen why this must necessarily be so, as was the case in the law of definite proportions.

### Exercises for Review

1. Name six different forms in which water occurs.

2. Give the characteristics of pure water. Why does it taste "flat"?

3. Give some idea as to the amount of water in the human body; also in many of our food products.

4. Explain how water aids in digestion and assimilation; also how it aids in warming the body and equalizing temperature in summer.

5. Describe the experiment showing analytic proof for composition of water. Explain why the oxygen collects at the anode.

6. Outline the experiment for proof of composition of water by weight.

7. State the "Law of Definite Proportions." Illustrate.

8. What is a hydrate? Water of combination? Give examples of hydrates.

9. Define efflorescence. What is the cause of it? What is a manometer? Give some experiment using a manometer and its purpose.

10. Define deliquescence. Name four deliquescent compounds. What use?

11. What is a hygroscopic substance? Why does salt become damp in wet weather?

12. How do cisterns and wells become contaminated? Why are rivers apt to be purer than cisterns in a city? How are river waters clarified?

13. What often occurs in small lakes used for water supply? How treated?

14. Compare water and hydrogen peroxide. Give uses of latter.

15. Give method of testing hydrogen peroxide.

16. State "Law of Multiple Proportions." Illustrate.

## CHAPTER III

## OXYGEN AND OZONE

**Outline—**

- Abundance of Oxygen in Nature
- Preparation in Laboratory
  - Catalysis
- Characteristics
  - (*a*) Physical
  - (*b*) Chemical
- Uses of Oxygen
  - (*a*) Respiration
  - (*b*) Combustion
  - (*c*) Medical and Others
- Oxidation, Combustion, Explosion
- Ozone, its Relation to Oxygen
- Preparation of Ozone
  - (*a*) In Laboratory
  - (*b*) For Commerce
- Characteristics
  - (*a*) Physical
  - (*b*) Chemical
- Uses

1. **Abundance of Oxygen.**—Oxygen constitutes about 50 per cent of all terrestrial matter. Of water it is eight-ninths by weight; of the rocky crust of the earth, such as limestone, sand, sandstone, it is practically 50 per cent; of the air about 23 per cent by weight; of the human body about two-thirds. Thus it is by far the most abundant of all the elements. Fig. 9 gives approximately the relative amount of oxygen and the seven other elements which constitute the greater part of the material of the earth.

2. **Preparation.**—As far as known, Scheele, a Swedish chemist, first prepared oxygen about 1773, using man-

ganese dioxide and sulphuric acid. However, he did not publish any account of his experiments for several years, and in the meantime Joseph Priestley, an English chemist, had in August, 1774, prepared and studied oxygen, making it by heating red mercuric oxide. It is interesting to know that he used as his source of heat a large lens or burning glass to concentrate the sun's rays and instead of the modern test tube he had a sawed-off gun barrel. Both of the above methods are still sometimes used, but there are much better ways. The most common method for obtaining oxygen in the laboratory is by heating potassium chlorate, mixed with manganese dioxide. The first named compound furnishes all the oxygen, although both contain it, but

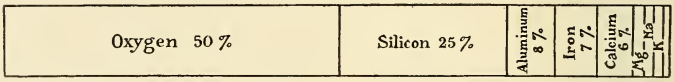



Fig. 9.—Showing relative abundance of oxygen in nature.

much less heat and time are needed if the mixture is used. By putting equal amounts of potassium chlorate into each of two test tubes and adding to one a small quantity of manganese dioxide, it is interesting to note that the mixture will give the oxygen test at the mouth of the tube in from one-sixth to one-fourth the time that is required for the other. Chemical tests show that the manganese dioxide is *unchanged* and may easily be recovered from the remaining mixture and used again. The action of any substance in thus hastening a chemical change is called *catalysis,* and the agent itself a *catalyst* or a *catalytic* agent. Many such cases will be observed from time to time in our study of chemical reactions. For example, it has been stated that hydrogen peroxide is a very unstable compound and owes its value to the fact of giving

off oxygen so readily. The addition of powdered metals or of charcoal, even in weak solutions, causes rapid decomposition of the peroxide. In a *polished* platinum dish a concentrated solution shows little evolution of oxygen, even at temperatures considerably above that of the ordinary room; but if the dish be roughened or scratched the decomposition becomes rapid. In all these cases, the powdered metals, the charcoal and the roughened platinum serve as catalytic agents in hastening the decomposition.

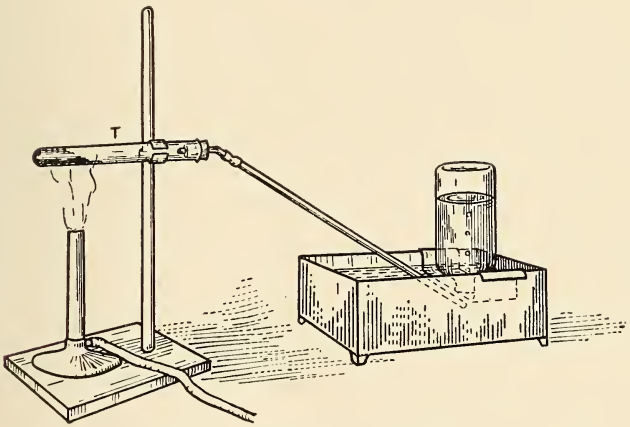



Fig. 10.—Preparation of oxygen.

The laboratory method of setting up the apparatus and of collecting the gas is shown in Fig. 10. The method is called *collecting over water*, and all gases not soluble in water may be collected in this manner. One precaution must be rigidly observed and that is, to remove the delivery tube from the water before taking the heat away from the generator. A third method often used when only small quantities are wanted is by allowing water to drop slowly upon sodium peroxide, a compound sold under the

name of "oxone." It gives off oxygen on the addition of water just as does hydrogen peroxide spontaneously.

3. **Characteristics of Oxygen.**—Physical.—Oxygen is an odorless gas, slightly heavier than air, and in small quantities, is colorless. When liquefied, as it may be at 182° C. below zero, it is of a distinctly blue color. It is possible that what we speak of as the *blue sky* may be the color, at least in part, of the great depth of oxygen. It is soluble in water; at 20° C., to the extent of 3 c.c. in 100, and in ice water about 4 c.c. in 100. In the liquid form

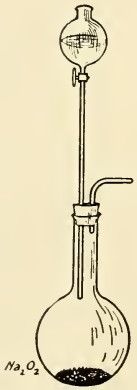



Fig. 11.—Preparing oxygen from sodium peroxide.

it is distinctly magnetic, as is shown by a suspended test tube of it being strongly attracted by a magnet. It may be solidified by surrounding with liquid hydrogen and is then a pale blue solid.

*Chemical Characteristics.*—The most important chemical property of oxygen is the vigor with which it combines with a large number of other elements, forming oxides. Charcoal, heated to redness, and lowered into a bottle of oxygen, glows brightly and if made from soft wood, it bursts into sparks. Phosphorus, ignited, in

a deflagrating spoon, in oxygen burns with dazzling brightness, while iron in the form of wire or a watch spring burns with a beautiful shower of sparks. Sulphur and zinc both burn much brighter than in the air. All of these are additive reactions in which oxygen has combined with another element forming an oxide. Usually upon the sides of the bottle, in which the watch spring is burned, will be seen a reddish deposit of iron oxide, like rust, but most of the iron has been converted into what is called magnetic oxide and has dropped to the bottom of the bottle in the molten condition. The charcoal, being largely carbon, has produced carbon dioxide, and so on. Many of the oxides, like the one formed from sulphur, when dissolved in water give an acid test, and this fact gave oxygen its name, from the Greek words meaning *acid former*.

4. **Uses.**—First of all should be mentioned its need in respiration. Aquatic animals breathe the small quantity of free oxygen dissolved in water, while land animals use the more concentrated form found in the air. Next to its value in respiration is its use in combustion. Ordinary fire is impossible without oxygen; and without fire man must have remained little more than a savage. He could hardly have passed the advancement of the stone age; the reduction of metals from their ores; the making of steel tools; the locomotive, the steamship, the automobile, the airplane, all would have remained forever beyond him. Besides these two great uses there are many minor ones. The oxygen helmet is often used by firemen to enter places impossible otherwise; by divers in exploring sunken vessels and for other undersea work; by rescuers after explosions in mines. The pulmotor is now a common appliance in the hospital, for inducing artificial respiration at critical times, such

as cases of asphyxiation, drowning, electric shock, and in crises of some diseases.

5. **Oxidation.**—The uniting of oxygen with any substance is called oxidation, although, in the broadest sense, to the chemist the term means much more than this. The action may be slow, or so rapid as to be accompanied by the generation of much heat. If sufficiently rapid to cause noticeable heat and light it is called *combustion,* but we shall see that combustion often takes place between substances when neither one is oxygen. Some substances, for example, oily waste or rags, absorb oxygen from the air: oxidation begins, and often sufficient heat is produced to ignite the rags. This is *spontaneous combustion.* It is never safe, therefore, to leave waste saturated with oils, especially drying oils like linseed, exposed long to the air. The manufacturers of the familiar cedar mop and others of like character, who use some kind of oil upon the cotton thread, provide a metal box to enclose the mop when not in use. At almost every coal mine, the dump is seen to be on fire. Certain iron compounds, when wet by rains and exposed to the air, begin to oxidize; the temperature rises and eventually is sufficiently high to ignite the small quantities of coal thrown out with the waste material. The fires in coal bins on shipboard probably often occur in the same way. A simple experiment illustrating spontaneous combustion may be made by dissolving a piece of yellow phosphorus the size of a pea in a cubic centimeter of carbon disulphide and pouring the solution on a filter paper resting upon a ring stand. As soon as the carbon disulphide has evaporated, which will be in a few seconds, oxidation begins, followed very quickly by the ignition of the phosphorus. An instantaneous or nearly instantaneous combustion is called an *explosion.* In all cases the to-

tal amount of heat produced is the same: in slow oxidations it is dissipated as fast as formed; in explosions, the whole generated in an instant of time, causes enormous expansion of all gases produced and, as a result, tremendous pressures and often frightful results.

6. **Kindling Temperature.**—The point at which combustion begins is called the kindling temperature. For phosphorus this is very low; for iron very high, with a great variety in between these two. A bit of yellow

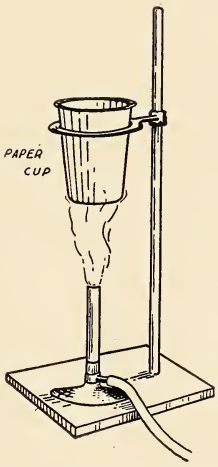



Fig. 12.—Boiling water in paper cup.

phosphorus exposed to the air soon reaches its kindling temperature; a pile of shavings needs but the heat of a burning match; while anthracite coal must be furnished much kindling before it will burn. A little experiment giving some idea of the kindling point of paper, not essentially different from that of shavings, may be made by boiling water in an ordinary sanitary paper drinking cup, as shown in Fig. 12. In a few minutes the

water will boil vigorously, but as the temperature of the paper is not greatly above that of the boiling water it does not catch fire.

## Ozone

7. **What Is Ozone?**—Ozone is an unusual form of oxygen, always produced when an electric discharge takes place in oxygen or in the air. It is noticeable about the open arc in stereopticon work, in wireless telegraphy, and all similar places. The word ozone is from the Greek, meaning *to smell* and was given this gas because of its peculiar odor. It is often spoken of as an *allotropic* form of oxygen, which means another form. Many substances appear in two or more distinct forms almost as different from each other as if they were not related at all; usually the rarer one, or more, are spoken of as the allotropes of the other, or the allotropic forms.

8. **Preparation of Ozone.**—To secure sufficient ozone for a test, a stick of freshly scraped phosphorus partly submerged in water in a bottle is generally used. For the test, a strip of white paper dipped in some starch mucilage, to which has been added a very little of a solution of potassium iodide, is suspended in the bottle. In a short time the paper turns blue. The ozone has united with the potassium, has set the iodine free, and this has formed a solution with the starch which has a blue color. It is believed that ozone is also produced by other slow oxidations. It is probable, that, being a form of oxygen, ozone is always produced in the preparation of oxygen by any method. However, as we shall see later, ozone is a very unstable body, and if much heat is needed or produced in the method used for preparing oxygen, most of the ozone will be decomposed al-

most immediately into ordinary oxygen. By the methods already suggested for the preparation of oxygen, by heating mercuric oxide or potassium chlorate, practically no ozone is obtained. But if a method is used involving the application of no heat and in which no high temperature is reached through the chemical action, appreciable amounts of ozone ought to be present. Such a method may be tried by adding a few drops of strong sulphuric acid to a solution of potassium permanganate

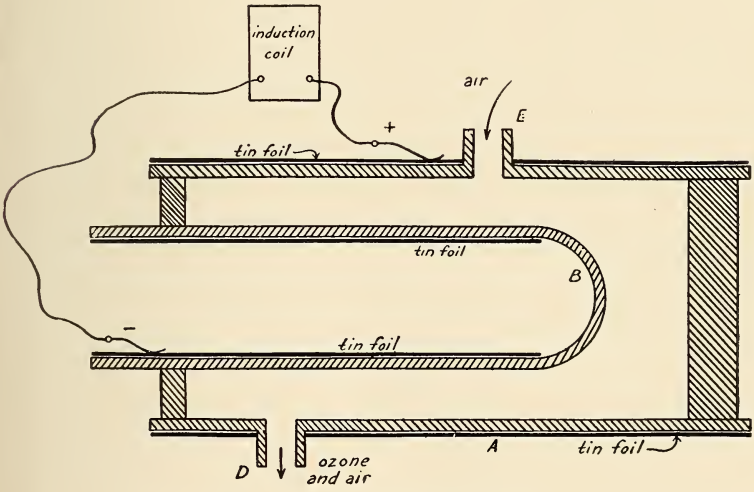



Fig. 13.—Machine for making ozone.

in water. The bubbles of oxygen may be seen coming up through the solution and the odor of ozone may be readily distinguished, often being sufficiently strong to irritate the throat. For commercial purposes ozone is now prepared by means of apparatus illustrated in Fig. 13. The current from an induction coil spreads over the tin foil coating on the outside of the outer tube through which a stream of oxygen or air is slowly flowing, as indi-

cated by the two arrows at E and D. The electricity by *brush* discharge passes across to the tin foil coating on the inner surface of the other tube and out over the return wire. Thus, by a silent discharge of the current, little heat is generated and a very appreciable quantity of ozone is present in the escaping current of air.

9. **Characteristics.**—*Physical.*—As already mentioned, ozone has a peculiar odor and is irritating to the throat and bronchial tubes, if present in considerable quantities. It is blue in color. It is much more soluble in water than oxygen; at 12° C. 100 c.c. of water will dissolve about 50 of ozone, while even at zero only 4 c.c. of oxygen would be dissolved by the same volume of water. Ozone is also very soluble in turpentine and this method is sometimes used to isolate it from other gases. Having a density one and a half that of oxygen indicates that three volumes of oxygen have been condensed to form two of the allotropic form. It liquefies at −119° C. If a current of ozone mixed with air be passed through a tube surrounded by liquid oxygen, the ozone is readily liquefied, while most of the oxygen will escape as a gas. Liquid ozone is deep blue in color and not transparent like liquid oxygen.

10. **Chemical Characteristics.**—The most important chemical property of ozone is its strong oxidizing power; it is also very unstable. Mercury and silver both remain untarnished in pure air, but in ozone they are quickly darkened. It attacks many other substances much more actively than does ordinary oxygen.

11. **Uses.**—Ozonized air, prepared as described in a preceding section, is now used in many photoplay houses of our cities as a means of vitalizing or purifying the air. Theoretically, it would seem to be an excellent plan, but in real practice there seems to be much doubt

on the part of some as to its efficiency. In some large flour mills, the wheat, after scrubbing, is passed still damp through ozonizers for destroying any traces of smut or mildew not removed by previous processes of milling. In some cities of Europe, ozone is used as is liquid chlorine in this country for purifying the water supplies. It is claimed that a gram of ozone, which if pure would be only about a half liter, or one pint, is sufficient to destroy as many as 30,000 bacteria per cubic centimeter in 1,000 liters, or 250 gallons. As there are 1,000 cubic centimeters in a liter, this would mean that a half liter of ozone or an equivalent mixed with air bubbled slowly through 250 gallons of water, would be sufficient to destroy thirty billion bacteria.

### Exercises for Review

1. What part of the earth's crust does oxygen form? Give its proportions in several familiar things.

2. What two men first prepared oxygen? What did they use?

3. What is the usual method in the laboratory? Define catalysis. Name some other instance of catalytic action.

4. Give its chief physical and chemical characteristics. How did it receive the name oxygen? What other names was it known by in an early day?

5. Name the most important uses of oxygen. Give five minor uses.

6. Define oxidation, combustion, explosion. How can you account for spontaneous combustion? Give some case where caution must be exercised about the home.

7. What is meant by the kindling temperature of a substance? Name one substance with very low kindling point: one with very high.

8. Has water a kindling temperature? Give reason for your answer.

9. What is ozone? Origin of its name? What is an allotrope?

10. Give two ways of preparing ozone and method of testing its presence.

11. How is ozone prepared on a large scale?

12. Compare ozone with oxygen.

13. Give three uses of ozone.

14. When a bellows is used to cause a fire to burn faster, is the action catalytic? Explain.

# CHAPTER IV

## HYDROGEN

**Outline—**

History of Hydrogen
Occurrence
Preparation
  (*a*) From Water
  (*b*) From Acids
  (*c*) From Oils
Characteristics of Hydrogen
  (*a*) Physical
  (*b*) Chemical
Practical Uses
The Phlogiston Theory of Combustion

1. **History.**—It is presumed that Paracelsus, the great physician-chemist in the sixteenth century, discovered hydrogen, for he carried out experiments that involved the preparation of it. But he records no facts regarding it and may have overlooked it entirely. In 1766, Cavendish, an English chemist, prepared hydrogen and recognized it as a new substance but did not consider it an element. He called it *inflammable air*. Later when it was discovered that in burning, it produces water, it was given its present name which is from the Greek, meaning *water producer*.

2. **Occurrence.**—It has been stated that hydrogen ranks ninth in abundance among the elements. In many ways, however, it is an important element. It constitutes as previously seen, one-ninth of the weight of water; it is an important constituent of nearly all organic matter such as oils and fats, sugars, starches and the like; also of all acids, many of which are already

familiar to the student. For example, acetic acid in vinegar, citric in lemons and grape fruit, oxalic in rhubarb as well as several others, are well known. In the laboratory the most common acids are hydrochloric, sulphuric and nitric.

3. **Preparation from Water.**—The preparation of hydrogen by the electrolysis of water has already been described. With the ordinary laboratory apparatus it is a slow process, but the gas obtained is very pure and sometimes this fact overbalances the lack of rapidity. Hydrogen may also be prepared from water by treating with some metal, as sodium or potassium. It may seem strange that a metal could do this. It has been seen already that hydrogen belongs among the electropositive elements. It must be stated, however, that some elements are much more positive in their behavior than others. Without attempting to be very exact, the elements may be arranged and compared to the parts of a bar magnet, as illustrated in Fig. 14. If the magnet is laid down upon a sheet of paper upon which iron filings have been sprinkled, most of the filings will be attracted to the ends which are called the poles of the magnet, with the quantity rapidly diminishing toward the center. In a similar way the elements may be arranged in the order of their electropositive character, and those the better known to the student are thus shown in Fig. 14. It will thus be seen that hydrogen is well down the list. Naturally, therefore, such elements as potassium and sodium would be presumed to have the power of taking a negative element away from hydrogen and setting it free. Experiment shows that potassium does this violently, such that even on cold water the hydrogen set free is ignited almost instantly and unless the piece of potassium is very small even it will burst into

pieces from the heat generated. Sodium, though much less active, decomposes water rapidly, but unless the water is warm the hydrogen is not ignited. With magnesium the water must be hot for even moderate results. In using sodium, since the metal melts almost

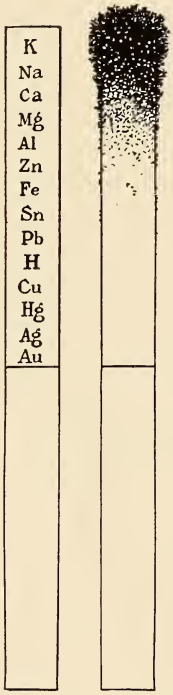



Fig. 14.—Electromotive series of metals and bar magnet with iron filings attached.

instantly when it touches the water, because of the heat generated by the chemical action, a gauze spoon is employed as shown in Fig. 15. The sodium is enclosed in this, inserted under the mouth of the test tube or bottle, which is filled with water and inverted over a

trough of water, whereupon the gas rises and fills the bottle. It is a method somewhat expensive, but the gas obtained is pure.

4. **Obtaining Hydrogen from Acids.**—As hydrogen may be expelled from water so it may be from acids, in a similar way and for the same reason. A very considerable number of metals might be used. Sodium and potassium would do, but their action is dangerously violent; hence, it should not be attempted. It is customary to use some metal much farther down the electromotive series, whereby the action is much slower. In the laboratory zinc is most often used either with hydrochloric or sulphuric acid diluted. Iron is cheaper and is used when large amounts are desired, but the gas is not so pure as when zinc is employed. The metal in mossy form, is put into the generating flask and barely covered with water. When the receiving bottles are ready in the trough, the acid is added through the thistle tube a little at a time until action begins. The thistle tube must dip below the surface of the water in the flask (Fig. 16).

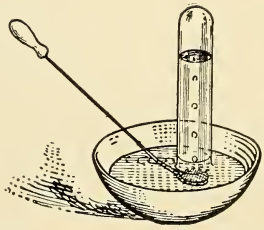


Fig. 15.—Preparing hydrogen from water by means of sodium.

5. **Preparation of Hydrogen from Oils.**—It is possible by heat alone to obtain hydrogen from such oils as kerosene and similar oils, prepared from crude petroleum

by distillation. But the gas thus obtained is only about 50 per cent hydrogen, the remainder being a variety. Yet for some purposes even this is sufficiently pure and is exceedingly cheap.

6. **Characteristics of Hydrogen, Physical.**—Hydrogen is an odorless, colorless gas, the lightest known. It is only about one-fourteenth as heavy as air, so that something over 11 liters are necessary to weigh 1 gram. It is a fairly good conductor of heat, which cannot be said of any other gas. It may be liquefied at a temperature of about −252° C. in which condition it is colorless. At −256° C. it becomes a solid. One of the most

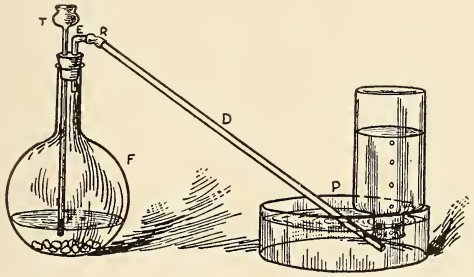



Fig. 16.—Preparation of hydrogen from acids.

interesting of its physical properties is its ability of being absorbed by certain metals with the evolution of heat. This may be shown by the platinum sponge held over a jet of escaping hydrogen. In a very few seconds the sponge becomes red-hot and the hydrogen is ignited. It may likewise be shown by lowering the sponge into a bottle of hydrogen and oxygen mixed in about the proportions of 2 to 1. The sponge quickly becomes red and the gases explode violently. There is no danger, however, if a wide mouthed bottle is used. This property is often called *occlusion*. Palladium has

more remarkable powers for absorbing hydrogen than has platinum, in that it will take up nearly seven hundred times its own volume of the gas. Hydrogen readily passes through unglazed porcelain and cracks in bottles which would not leak water, and a cork made of plaster of paris is so porous as to offer little obstruction to the escape of the gas. For the same reason, toy balloons soon lose their buoyancy.

7. **Chemical Characteristics.**—Hydrogen burns with a very pale blue flame with intense heat. If the delivery tube be glass, it is soon heated to redness, when the flame becomes visible, because of the constituents of the glass giving a yellow color. One gram of hydrogen in burning will produce more than four times as many

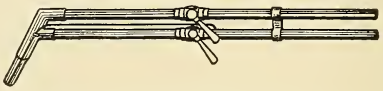


Fig. 17.—Oxyhydrogen blowpipe.

heat units as the same weight of anthracite coal. Water is the sole product of combustion.

8. **Practical Uses.**—One valuable use is in the oxyhydrogen blowpipe or torch as it is often called. It is illustrated in Fig. 17. The hydrogen enters through one pipe and the oxygen by the other, and near the point where ignited they are thoroughly mixed. The stopcocks are so opened by the operator as to furnish twice as much hydrogen as oxygen. Intense heat is thus obtained, ranging in temperature from 2,000° to 2,500° C., at which platinum and other refractory metals are readily melted. If this flame be allowed to impinge upon a stick of lime, it gives a dazzling white light, called the *calcium* or *Drummond light*. Up to the introduction of

the electric arc, this was the best and commonly used light for stereopticons and stage effects. Another use for hydrogen is in filling balloons. Especially during the world war was this extensive for dirigibles and for observation balloons. For some purposes natural gas may be used and has often been in flight contests, but it is eight times as heavy as hydrogen, hence does not compare in efficiency. However, its loss through diffusion would be much slower. For short flights, such as those seen at amusement parks and the like, the balloons are usually filled by heating kerosene or naphtha, as suggested in a preceding section. As this is often done by spraying the oil upon a bed of hot coals, there is usually some small amount of air present and some imperfect combustion resulting in the formation of some smoke. For this reason, when the aeronaut leaps from the car in the parachute, a puff of smoke is often seen emerging from the capsized balloon.

9. **An Old Theory of Combustion.**—Combustion is now well understood, but during the last quarter of the eighteenth century it was a matter of constant study and of much dispute. With the exception of Lavoisier, who lost his life at the time of the French Revolution, practically all the chemists of that day accepted the theory that a substance called *phlogiston* was contained in every combustible substance, and that it escaped as the substance was burned. The great French chemist never accepted this theory; and finally by the use of the balance, which up to that time chemists had not employed to any great extent, he succeeded in showing the fallacy of the phlogistic theory. It is now known that when a metal or any substance is burned, if all the products of combustion are saved and weighed, the total is greater than the weight of the original substance. Lavoisier called attention to this fact, and argued that if something

escaped, the resulting oxides, or *calces,* as they were called in that day, ought to weigh less. The upholders of the theory replied that, since phlogiston is an exceedingly light substance, it has a buoyant effect upon whatever contains it, and therefore, the more there is the

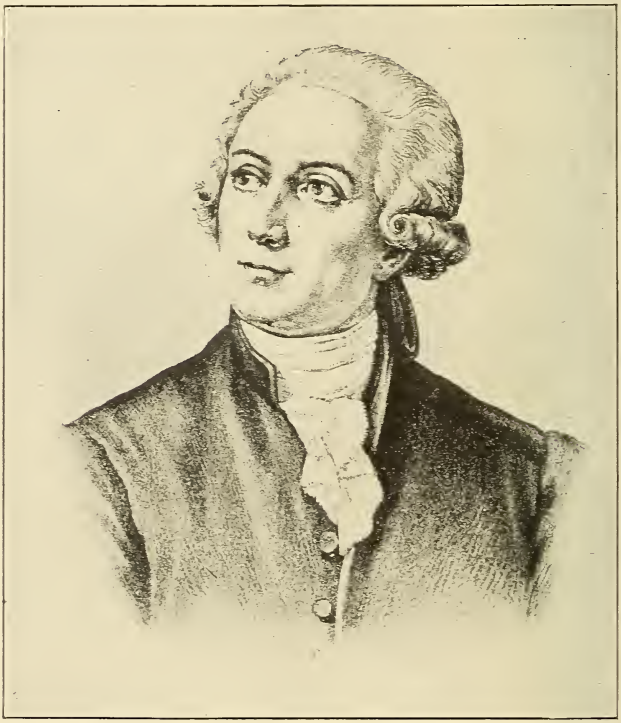


Fig. 18.—Lavoisier, beheaded in French Revolution, was the Father of Modern Chemistry.

lighter the object. When hydrogen was discovered and its extreme lightness noted, as well as its great combustibility, many of the phlogistonists believed they had discovered phlogiston and regarded it as upholding their

theory. But, in the light of what the balance continually showed, they were finally obliged to acknowledge the fallacy of their position and that Lavoisier was correct.

### Exercises for Review

1. Give a brief account of the discovery of hydrogen. How did it come to receive its present name?

2. Name some very common substances containing hydrogen. How does it rank among the elements in total amount?

3. Give two ways of obtaining hydrogen from water. What can be said about the value of these methods?

4. What do you understand by the electromotive series of metals? Where does hydrogen come in this series?

5. How may hydrogen be obtained from acids? What metals are best? Why? What acids are generally used? Would nitric do?

6. How may hydrogen be obtained from kerosene or gasoline? What is true of the purity of the gas thus obtained?

7. Give the chief characteristics of hydrogen. Explain what is meant by occlusion. Give two experiments to illustrate.

8. Give three important uses of hydrogen. What is the Drummond light?

9. Give briefly the phlogiston theory of combustion. What was the most absurd thing about this theory? Who finally overthrew it?

## CHAPTER V

## THE ATMOSPHERE

Outline—

- Early Ideas of the Air
- Composition of Air
  - Proportions
- Proof that Air is Mixture
- Diffusion of Gases
- Ventilation
- Purposes of the Constituents
  - (*a*) The Oxygen
  - (*b*) Nitrogen
  - (*c*) Carbon Dioxide
  - (*d*) Water Vapor
- Humidity and Health
- Liquid Air
- Argon and Helium

1. **Early Ideas of the Air.**—Even before the beginning of the Christian era the air was an object of interest among philosophers. For centuries thereafter, however, little advancement was made in the knowledge concerning it, for the reason that no experimental study of it was attempted. In the latter part of the eighteenth century when the phlogiston theory was at its height a very considerable number of gases was discovered and the air itself received a very careful study in its relation to combustion. Even thus, until near the end of the century, all the gases known were regarded as modifications of atmospheric air and were named accordingly. Thus, Cavendish called hydrogen *inflammable air;* Scheele called oxygen *fire air;* Priestley named it *dephlogisticated air;* Black, the discoverer of carbon dioxide called it *fixed air;* nitrogen was known as *azote*

or *phlogisticated air* and so on. As we have seen it was Lavoisier who overturned the prevalent ideas and suggested suitable names for some of the gases of recent discovery.

2. **Components of the Air.**—In what is often spoken of as pure air there are always found nitrogen, oxygen, argon, carbon dioxide and water vapor, besides minute quantities of a few very rare elements. Sometimes the first three of these are regarded as the atmosphere proper, for the reason that they vary little; but when the evident purposes of the air are considered, the other two are essentials, and in the following study will be regarded as constituents. For years the air was believed to contain the two main gases in the form of a compound. At that time, the presence of argon was not known and the apparent unvarying proportion of oxygen and nitrogen led chemists to believe they were in combination.

3. **Proportions of These Constituents.**—By volume the oxygen in the air constitutes about 21 per cent; the nitrogen, 78 per cent; the argon, a little less than 1 per cent—0.94—and the carbon dioxide, about .03 per cent, with the water vapor decidedly variable. If the air were of the same density throughout, it would extend above the surface about five miles. Then if the various constituents were arranged in layers about the earth, in accordance with their respective densities, there would be nearest the ground a layer of water about 5 inches deep; above that, one of argon, about 250 feet deep; then carbon dioxide, 12 or 13 feet; above that, oxygen one mile, and lastly the nitrogen, four miles.

4. **Proof That Air Is a Mixture.**—There is very strong and convincing evidence now that air is a mixture. When pure distilled water is exposed to the air, al-

though the amount of nitrogen is about four times that of the oxygen, the oxygen absorbed is nearly double that of the nitrogen. If the air were a compound, the absorption of the two gases would necessarily be in the proportion in which they entered into the compound. Again, air is now readily liquefied. When this happens the carbon dioxide and the water vapor solidify and precipitate out. A vessel of liquid air left standing shows, when about four-fifths of it has boiled away, that the residue is nearly pure oxygen. This would be possible only if the air were a mixture and the boiling point of nitrogen lower than that of oxygen. Alcohol in boiling gives off vapor of the same composition as the liquid and so does every liquid compound. Air, therefore, cannot be a compound. Again, every compound consists of two or more elements in unvarying proportions. In the air the oxygen may vary as much as three-fourths of 1 per cent. Not only these, but other proofs make it sure that the air is a mixture and not a compound.

By weight the constituents are—

| | |
|---|---|
| Nitrogen | 75.46 per cent |
| Oxygen | 23.18 " |
| Argon | 1.29 " |
| Carbon Dioxide | .03 to .04 " |
| Water Vapor | Variable |
| Other rare Gases | Very small amounts |

5. **Diffusion of Gases.**—If in a tall cylinder nearly filled with water, colored blue with litmus, a few cubic centimeters of sulphuric acid be introduced below the water by means of a pipette, in two or three days the heavy acid will have moved upward through the entire mass of water. This will be known by the litmus solution turning red, as it does in the pres-

ence of any acid. Likewise any gas tends to occupy all the space afforded it. If a cylinder of ammonia be inverted over one of hydrogen chloride, although the lighter gas is above one more than twice as heavy, in a very few minutes the two will be evenly distributed throughout the entire space, as can be seen by the action which takes place. This shows that the particles of a gaseous body are apparently moving in all directions all the time regardless of their density. This explains largely why the air is always a practically uniform mixture. Equilibrium is constantly being destroyed by various processes of nature and otherwise, but *diffusion,* as this movement is called, aided by wind currents, keeps the composition practically constant.

6. **Value of Each Constituent.**—It has been stated in a preceding chapter that oxygen is necessary for respiration. When taken into the lungs it enters into a loose combination with the hemoglobin and is by the circulation taken throughout the body. Meeting the carbon in the various tissues, carbon dioxide is formed and by the oxidation heat is produced. Thus the body is warmed. In aquatic animals where the only oxygen attainable is the small amount dissolved in the water, the quantity of carbon consumed in the tissues is small, and thus little heat is produced. Such animals are "cold blooded"; naturally, therefore, the food required to sustain life is small in proportion. A good comparison may be had by noting the amount of food consumed by a canary bird and a gold fish of about the same weight. The human body of average size consumes daily about 750 grams or 26 ounces of oxygen. This is the equivalent of the entire amount of oxygen contained in over 2,600 liters of air. From this is produced carbon dioxide to the amount of about 2.2 pounds or

1,000 grams. When the air leaves the lungs at each respiration only about 16 per cent of oxygen remains instead of the original 23 per cent, while the carbon dioxide in the exhaled breath is present to the extent of about 4.4 per cent or more than 100 times as much as is contained in ordinary air.

7. **Ventilation.**—It is apparent from the above how important good ventilation becomes. This importance is emphasized when it is remembered that while the first respiration of a given volume of air removes over one-fourth of the oxygen, the second inhalation of the same volume of air only takes about the same proportion of what remains. Thus the body in obtaining impoverished air is not receiving anything like the amount needed. Lack of proper ventilation is most apt to be found in school rooms or other places where people congregate in considerable numbers, as photoplay houses, theaters, and the like. Health boards in many cities require that means shall be provided for furnishing 30 cubic feet of fresh air per minute per individual. In the ordinary home where the family is small there is no special provision needed, for even in cold weather when doors and windows are closed there is sufficient leakage to furnish an abundance of fresh air. It is only in poor tenement houses and basements used as homes, where large families are often found, that the lack of ventilation is apparent in the home.

8. **Value of the Nitrogen.**—To the human body, nitrogen, as it exists in the air in a free state, seems to serve no other purpose than to dilute the oxygen. A fish out of water dies, partly probably because of the very rich atmosphere it is compelled to breathe. In the same way the human body, as at present constituted, could probably not inhale pure oxygen continuously without un-

due stimulation and serious results. In the combined form nitrogen enters into the muscular part of the body and only through the use of nitrogenous foods can its waste be repaired. Neither animals nor plants, as a general rule, can obtain nitrogen directly from the air, at least in sufficient quantities to meet their necessities. Animals secure it mainly through lean meats or leguminous foods such as beans, peas and the clovers. Most plants in continuously cultivated fields obtain their

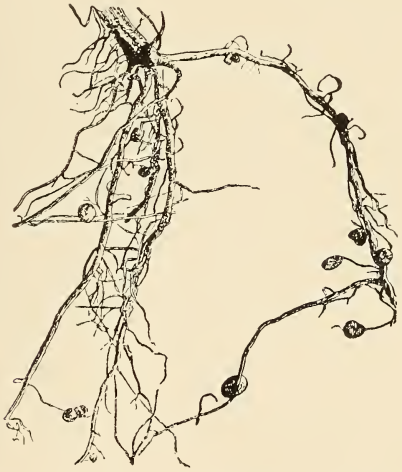


Fig. 19.—Nodules in which the nitrogen-fixing bacteria live on the roots of a bean. (From Warren—Elements of Agriculture.)

needed supply through fertilizers, which are largely obtained from the waste eliminated by the animal economy. So it will be seen there is an endless cycle existing here in which animals and plants each supplement the needs of the other. It should be stated, however, that there is one class of plants which, fortunately, is able through the aid of bacteria to obtain the nitrogen needed directly from the air. These are the legumes, and agricul-

turists at present are employing this means extensively in restoring the needed nitrogen to the soils. The accompanying figure shows the nodules upon the roots of a bean plant, formed by the nitrogen fixing bacteria. (Fig. 19.)

9. **Carbon Dioxide.**—It will be learned later that carbon dioxide is an inert gas as far as the human system is concerned, in that it is devoid of toxic effects. It is true, however, that a considerable quantity of it in the air usually indicates the presence of other substances deleterious to health. This is especially true if the air be impoverished by frequent respiration and therefore abounding in the waste materials thrown off from the body. It is this condition mainly that proper ventilation seeks to avoid. Health experiments carried out in such places as breweries, where considerable amounts of carbon dioxide are continually escaping into the air, show that, other conditions not being unfavorable, headache and drowsiness, usually apparent in poorly ventilated rooms, do not occur and no unfavorable results follow. To plants, carbon dioxide is as essential as oxygen to animals. The leaves, corresponding to the lungs of the body, absorb the carbon dioxide and under the influence of sunlight are able to decompose it. In the plant laboratory the carbon is combined with the water obtained from the soil and cellulose results to build the woody structure of the plant or tree. Another arrangement by another plant produces starch or sugar and a great variety of other well-known substances. But they all come primarily from the carbon dioxide obtained from the air through the leaves and must have the heat and light of the sun for the process. It is seen, therefore, as in the case of the nitrogen, that there is an endless cycle in the transference of carbon from the animal to

the vegetable world and back again, and that the existence of either without the other would in all probability not be of long endurance.

10. **The Water Vapor.**—It has been stated that the water vapor in the air varies greatly. The amount that can be held is dependent upon the temperature. At 0° C. a cubic meter, which is something more than a cubic yard, is able to hold only 4.87 grams of water: at 10° C. it can hold 9.92 grams; at 20°, which is but little cooler than ordinary room temperature, 17.16 grams. For health, from two-thirds to three-fourths of the amount specified at room temperature is regarded as best; more than this, if the temperature be high, is oppressive. The reason is that the human body regulates its temperature by the evaporation of water through the pores of the skin. A single gram of water for its evaporation requires something like 550 calories of heat; an ounce of water, which is about 28 grams, in being evaporated from the surface of the human body, would reduce the temperature of the entire body of 150 pounds weight about .5 of a degree. Anything therefore, which prevents or retards evaporation prevents the cooling of the body. When the humidity is high, as it often is in summer in the Atlantic, Gulf and Mississippi Valley states, the air surrounding the body is already nearly saturated with moisture. This greatly retards evaporation, and interferes with the regulation of the body temperature.

11. **Moisture and Health.**—The public has been more or less well informed as to the importance of fresh air; but the humidity of the air in the home in winter has not been greatly considered. As stated already, air at 0° C. or 32° F. can hold only 4.87 grams of water vapor. Usually there is present not one-half this amount. This

air is taken into our homes, warmed to 20° or 21° C. or about 70° F., without the addition of any appreciable amount of water. The result is a condition decidedly adverse to health. Unduly dry nasal passages, irritated throat and bronchi, susceptibility to colds, chapped hands and skin and other evils follow. The question of humidity is now carefully considered by architects in the construction of large school buildings and the moisture content of the air is kept reasonably uniform by artificial means. In the homes like provision should be made. As it is not provided by the usual methods of construction and heating, the individual must do this himself. In rooms heated by radiators, either steam or hot water, a towel suspended from a rack, fastened behind the radiator and dipping in a pan of water sitting on the floor, will be out of sight and will furnish ample moisture. With hot air furnaces the problem is more difficult. It may be partially met by putting shallow pans of water beneath each register where such are located in the floor. When not, each case with its possibilities must be taken up by itself. It is a problem the student should interest himself in for the benefit of everyone in the home.

12. **Liquid Air.**—For some years air has been liquefied in commercial quantities. The principle underlying is that ordinary gases expanding from great pressure into a more or less perfect vacuum are cooled. In the apparatus used, this cooled, expanded air is compelled to pass out around the pipe through which the compressed air is entering. Thus at each impulse of the pump, cooler and cooler portions of air are forced out around the incoming supply, until eventually the point of liquefaction is reached. It is a colorless liquid, like water, and usually consists of 50 per cent or more

of oxygen instead of 23 per cent as in the atmosphere. The reason is that the boiling point of nitrogen is 194° C. below zero, while that of oxygen is 11½ degrees higher. Thus from the constant loss of the nitrogen through evaporation the proportion of oxygen continually increases the longer the vessel stands. Liquid air is kept and shipped in what are called *Dewar* bulbs, shown in Fig. 20. They are the original of what the public knows as *thermos* bottles, being double-walled flasks with a vacuum between and the walls coated with silver.

13. **Argon and Helium.**—It has long been known that nitrogen prepared from the air is heavier than samples made from various nitrogen compounds. This led to

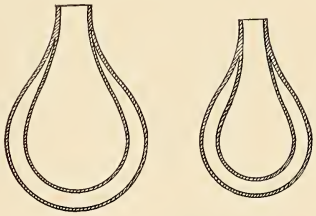


Fig. 20.—Dewar bulbs. The thermos bottle is merely different in shape.

the suspicion that there was some heavier gas mixed with it. Even as early as the latter part of the eighteenth century, Cavendish, the discoverer of hydrogen, was convinced that atmospheric nitrogen contained another gas and attempted to prove it experimentally. In eliminating the nitrogen he had as a residual gas only a small bubble which he concluded to disregard. He probably used too small quantities of air, for Ramsey, in 1894, by practically the same experiment succeeded in obtaining sufficient quantity of the argon to prove it was the same gas he had obtained by another method of separating it from nitrogen. It is an inert gas and

received the name "argon" from a Greek word, meaning *lazy* or *inactive*. No compounds of argon are known.

14. **Helium.**—The word is derived from the Greek for *sun,* and the name was given to this element because before it was known upon the earth a line in the orange band of the *solar* spectrum was observed which belonged to some undiscovered element. Later, it was discovered in certain spring waters; it may be obtained from certain minerals, compounds of uranium and thorium and is found in minute quantities in the air. It is a gas which is harder to liquefy than is hydrogen, having a boiling point of −268.5° C. It is only twice as heavy as hydrogen and unlike hydrogen is not combustible. It forms no known compounds. It is admirably adapted for filling balloons and dirigibles, and during the latter part of the war the United States was making great efforts at discovering some method of preparing it in commercial quantities. Not until too late was such a method devised. It is still a secret of the war department.

### Exercises for Review

1. Name some of the gases discovered during the latter part of the eighteenth century and the names applied to them. Why were they given such names?

2. Name the five components of the air. Give their proportions by volume and by weight. In what condition are they, free or combined?

3. Give three or four proofs that the air is a mixture.

4. What is meant by diffusion of gases? What effect does diffusion have on the homogeneity of the air?

5. What is the use of oxygen to the human body? Why are most aquatic animals cold blooded? Why is the whale not? Explain how the body is warmed.

6. How much oxygen is removed from the air at each respiration? How many cubic feet per minute are needed for an individual?

7. Of what use is the nitrogen of the air to the body? How are the muscles repaired? Describe the nitrogen cycle.

8. How are legumes different from most other plants? What gives them this power?

9. What do considerable quantities of carbon dioxide in a room indicate? Is it deleterious to health?

10. Describe the carbon cycle between plants and animals. What use do plants make of carbon? Of what use to animals?

11. What governs the amount of moisture the air can hold? What is meant by saturated air? How much more moisture can air at ordinary room temperature hold than at zero?

12. Why is a humid atmosphere oppressive in summer?

13. What effect does an excessively dry atmosphere have upon the body?

14. Give some methods of increasing the humidity in the home in winter.

15. Give the principle underlying the liquefaction of air. What is a Dewar bulb?

16. Describe liquid air.

17. How did argon come to be discovered? Who was first to attempt its discovery? Who finally discovered it?

18. How did helium receive its name? Where is it found upon the earth? Of what special value will it be in large amounts?

## CHAPTER VI

## GASES AND SOME GAS LAWS

**Outline—**

States of Matter
Charles' Law and Absolute Zero
    Applications of the Law
Boyle's Law
Correction for Changes in Temperature and Pressure
Aqueous Tension
Deductions from these Gas Laws
    (*a*) The Molecular Theory
    (*b*) Molecular Motion
    (*c*) Gas Pressures
The Atomic Theory
The Corpuscular Theory
Atomic and Molecular Weights
Avogadro's Hypothesis
Atomic Structure of Molecules
Determination of Molecular Weights
Gram Molecular Weight

1. **States of Matter.**—We are familiar with water in three conditions: solid—ice; liquid—water; gas, as steam. It has been stated in preceding chapters that oxygen, hydrogen and other gases may also exist in these three states. There are two forces present in every body: cohesion, an attractive force, tending to hold its particles together, and heat, a repellant force, tending to expand it, or to separate its particles. Hence, when heat is applied, first the body expands, then if capable of doing so, it melts, and on the continued addition of heat the liquid vaporizes with very great expansion. Removal of the heat reverses the process. In gases, therefore, the repellant force is in the ascendancy; in

solids, the cohesive force. Solids and liquids upon being heated expand very irregularly; but gases are practically constant and their behavior is described by certain clearly defined laws.

2. **Charles' Law.**—Experiment shows that any gas if heated from 0° C. to 1° above, expands 1/273 of its volume at zero. Thus, if at the beginning there were 273 c.c., at 1° C. there would be 274 c.c.; at 10° C. 283 c.c.; at 100°, 373 c.c. Likewise, if cooled below zero, at

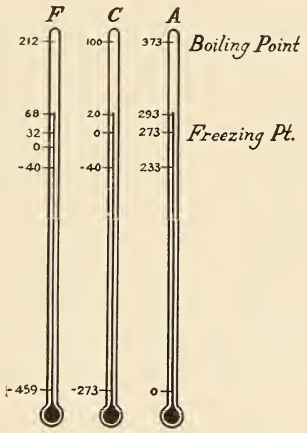



Fig. 21.—Comparison of thermometers.

−10° C., there would be 263 c.c. at 100° below, 173 c.c. Theoretically, therefore, if a gas were cooled 273° below zero its volume would have decreased to zero. But all gases become liquids before reaching this temperature; oxygen at −182.5°, hydrogen at −252.6°, helium at −268.5° and thereafter the contraction is very slight for each degree. The point, 273° below zero is known as *absolute zero.* While it does not mean the elimination of the substance, for that is unthinkable, it may be assumed

to mean the temperature at which there is no longer any heat in the body. In the liquefaction of helium, that point has been very nearly reached. It must be seen then that the volume of a gas varies as the absolute temperature. Charles' law states this fact thus: *The volume of a gas, pressure remaining constant, increases or decreases directly as the absolute temperature.* The absolute thermometer is not a manufactured article, but its degrees are the same as on the Centigrade scale, and it must be used in all problems involving Charles' law; hence Fig. 21 is given to make the method clear. Thus the boiling point of water would be 373° absolute and of melting ice 273° absolute.

3. **Value of Charles' Law.**—Gases for the sake of convenience are measured in volumes, but as they change greatly under varying conditions some standard must be adopted. For temperature this is the freezing point of water—zero Centigrade. However, as in actual work gases are seldom obtained at this temperature, their volume must be calculated from the measured volume. Knowing that they increase 1/273 for every degree raised above zero, this is not difficult. Putting Charles' law into a proportion we have

$$V : V' :: T : T'$$

In which V is the original volume and V′ the new volume, while T is the original temperature, absolute, and T′ the new temperature absolute. In the form of an equation this reads,

$$VT' = V'T$$

from which either volume or temperature may be calculated, knowing the other factors. To make the process clear, suppose we have in the laboratory a bottle hold-

ing 800 c.c. of oxygen, with the temperature 15° C. and without any change in pressure the temperature was raised to 22°. It is desired to know the new volume. Changing 15° C. and 22° C. to absolute temperatures, we have $273+15=288$ and $273+22=295$. Substituting we have

$$800\times 295 = V'\times 288$$

$$V' = \frac{800\times 295}{288}$$

from which the value of V′, or the volume at 22° will be known.

4. **Boyle's Law.**—It was formerly believed that liquids and solids could not be compressed; it is known now, however, that they may be, but as is true in variation of temperature they obey no law. Gases, on the other hand, are practically constant, a fact which was discovered by Robert Boyle and formulated by him in this law: *The volume of any gas, provided the temperature remains constant, varies inversely as the pressure.* Inversely means that if the pressure be increased the volume is diminished correspondingly and if the pressure be decreased the volume increases in the same ratio. Put into mathematical form it is stated thus:

$$V : V' :: P' : P$$

in which V and V′ have the same signification as stated under Charles' law and P and P′ are the original and new pressures respectively. In the form of an equation the proportion becomes

$$VP = V'P'$$

which leads to another statement of the law, thus: *The product of the volume of any gas multiplied by its pressure, always assuming that the temperature is constant, is a constant quantity.* To illustrate, suppose we have

200 c.c. of oxygen in a bottle at 15 pounds' pressure to the square inch. The product of the volume and pressure, $V \times P$, or $200 \times 15$, is 3,000. If the pressure be doubled, according to Boyle's law, the volume now would be 100. The product of $V'$ by $P'$, or $100 \times 30$ is 3,000, the same as before. Hence the statement that the volume of any gas multiplied by its pressure is always equal

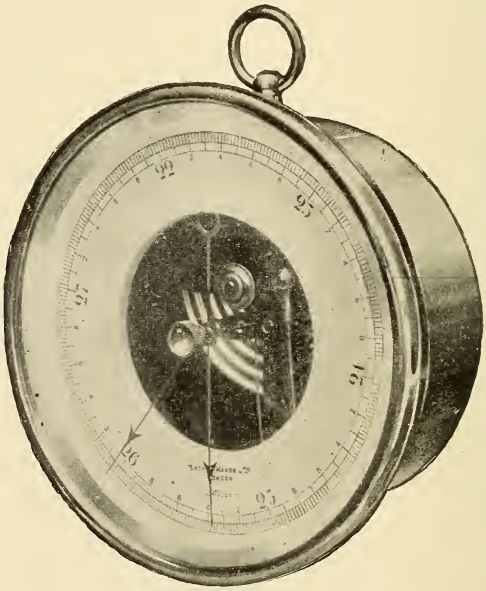


Fig. 22.—Aneroid barometer.

to its volume at any other time multiplied by the pressure at that time; in other words, the product is a constant quantity.

5. **Pressures, How Stated.**—In most practical problems involving Boyle's law the changes are those of atmospheric pressure only. The amount of such pressure is obtained by the use of the barometer, which for the

sake of convenience is read in units of length and not weight. In the aneroid barometer, shown in Fig. 22, the figures on the dial indicate inches, while the smaller divisions are millimeters of which practically 760 equal 30 inches. In the mercurial barometer at sea level, the pressure of the air supports a column of mercury 30 inches in height or, in other words, the weight of 30 inches of mercury. But as the *weight* of 28 inches of mercury would have the same mathematical relation to the *weight* of 30 inches of mercury as 28 inches to 30 inches, and as length can be read immediately from the barometer, in all problems it is customary to use linear units, and those of the metric system; that is, millimeters or centimeters. To illustrate: Suppose the barometer reads 750 mm. and we have in a bottle standing over mercury 500 c.c. of gas, and wish to know the volume at *standard* pressure, which means pressure at sea level, or 760 mm. pressure. Substituting in the formula,

$$VP = V'P',$$

we have

$$500 \times 750 = V' \times 760$$

$$V' = \frac{500 \times 750}{760}$$

in which $V'$ will be the true volume at one atmosphere's pressure.

6. **Corrections for Pressure and Temperature.**—In practical work often both pressure and temperature have changed during the time of an experiment. In such cases calculation must be made to correct both. This may be done in two steps, by finding the volume resulting from one change, either pressure or temperature, and then using this in the other equation. In fact beginners may find all such problems easier if solved by analysis instead of by use of formula given. At any

rate the method has the advantage of appealing to the reasoning powers at every step and on that account is good. It must be evident that increased pressure would cause decreased volume. Hence the original volume must be multiplied by a fraction greater or less than one as the change in pressure would cause increase or decrease in volume. Thus, if we have 500 volumes of gas at 760 mm. pressure and wish to know what it would be at 780, we must ask ourselves, whether the volume is increased or decreased. As the pressure is greater, the volume would be less: hence the original 500 cubic centimeters must be multiplied by 760/780 which will give a result less than 500. In the same way Charles' Law may be applied. Increase in temperature causes increase in volume. Thus, remembering that absolute temperatures are always used, suppose we have 500 c.c. of gas at zero Centigrade and wish to know its volume at 20 degrees above: we must first change Centigrade readings into Absolute. In this case they would be respectively 273 and 293. As the volume is increased the 500 c.c. must be multiplied by the fraction 293/273 which will give a value greater than 500. In case both temperature and pressure change, the result obtained in one of the above operations must be used as the original volume for the next.

It is somewhat simpler, however, to use a combined formula,

$$VPT' = V'P'T,$$

in which the letters mean as previously stated. To illustrate its use: Suppose we have 500 c.c. of hydrogen over a trough of mercury at a temperature of 21° C. with the barometer reading 740 mm. It is desired to know the volume at standard conditions, that is zero Centigrade and 760 mm. pressure. Substituting in the formula $VPT' = V'P'T$, we have

$$500 \times 740 \times (273 + 0) = V' \times 760 \times (273 + 21)$$

$$V' = \frac{500 \times 740 \times 273}{760 \times 294}$$

The value of V′ will be the true volume. In a similar way we might find the value of T′ or P′ or any other factor provided the others were known.

7. **Correction for Water Vapor.**—In the laboratory gases are usually collected over water and hence contain some vapor. To learn their true volume at standard conditions, correction must be made for this. It has been found that at any given temperature the vapor, passing off from an enclosed vessel of water, will exert a definite pressure, always the same for that particular tempera-

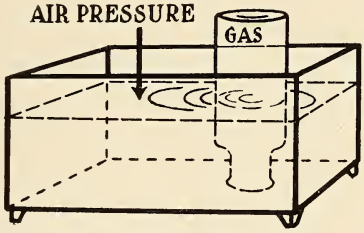



Fig. 23.—Illustrating pressure of water vapor.

ture. In Fig. 23, suppose we have a volume of gas with the water at the same level inside and without the bottle. Obviously the pressure within and without must be the same. On the outside the pressure is due to the weight of the air resting upon the water. Inside, the pressure results mainly from the gas enclosed, but partly from the vapor mixed with the gas. To know the real pressure of the gas, that of the vapor, which is spoken of as *aqueous tension,* must be subtracted from the total pressure. To illustrate: Suppose the gas in the bottle measures 900 c.c. and the barometer reads 750 mm., and the thermometer, 20° C. The aqueous tension at 20°

is about 17 mm.; hence, the pressure which the gas within the bottle is exerting is 750 minus 17 or 733 mm. Then, if it were required to find the true volume at standard pressure, the following substitution would be made in the formula, $VP = V'P'$

$$900 \times (750 - 17) = V' \times 760$$

The following table gives the aqueous tension for a short range of ordinary room temperatures.

| Temperature | Aq. Tension | Temperature | Aq. Tension |
|---|---|---|---|
| 16° C. | 13.54 mm. | 21° C. | 18.49 mm. |
| 17 | 14.42 | 22 | 19.66 |
| 18 | 15.36 | 23 | 20.88 |
| 19 | 16.35 | 24 | 22.18 |
| 20 | 17.39 | 25 | 23.55 |

8. **Application of these Laws.**—The gas in most cities is furnished by some company which is required by ordinance to maintain a certain pressure, say 6 or 8 inches, water pressure. If instead of doing this the company allow the pressure to drop to 4 or 2 inches or any lower pressure than that specified, it is, according to Boyle's law, furnishing the consumer an expanded gas; therefore, while the meter registers the larger amount the consumer only has the value contained in the real volume. It should be stated, however, that as the 6 or 8 inches required is necessarily the pressure in addition to one atmosphere or 30 water feet, a drop of 4 inches is not relatively large. Nevertheless, consumers should be furnished gas by the number of heat units contained and not by volume. The aeronaut must observe these gas laws in filling his balloon. Too great initial pressure, when he has ascended into a rarer atmosphere, and bright sunlight, may result in such increased pressure through expansion from the heat of the sun as to burst the balloon. On the other hand, too low initial pressure,

when night comes, with the great drop of temperature in the upper air may cause such contraction of volume that the buoyancy of the balloon will no longer support the attendant weight.

9. **Some Deductions.**—Cooling or heating a given volume of gas does not change its weight. Compressing, or the reverse, likewise, has no effect upon the weight; therefore, obviously by any of these changes we have not affected the real quantity of the gas. At sea level, the pressure of the air per square inch of surface is about 15 pounds. Now it is possible by modern appliances to obtain pressures approximating 150,000 pounds to the square inch. To some gases, such pressures as these may be applied and they are still gases unless the temperature is also greatly decreased: according to Boyle's law the volume has been decreased to one ten-thousandth part of what it was originally. In other words, the particles constituting the gas have been moved closer together, so that now they are only one ten-thousandth part as far from each other as they were at the beginning. Under moderate pressures, as we have seen, all gases behave alike; hence, there can be only one deduction and that is that all gases are composed of particles not touching each other; really, of particles at relatively great distances from each other. As all liquids may likewise be compressed, though but slightly and irregularly, their particles also must not be contiguous. This may be shown to be true by a simple experiment. If a liter cylinder be half filled with alcohol and then a like amount of water cautiously introduced beneath the alcohol by means of a pipette, at first there will be 1,000 c.c. of the two unmixed liquids (Fig. 24). Now, if by a stirring rod they are thoroughly mixed, the volume will be found to have decreased about 10 per cent. Like-

wise, considerable quantities of various solids like salt, or sugar or alum may be dissolved in a given volume of water without increasing the volume to any great extent. It is like pouring a pint of sand upon a quart of coarse shot. By adding the sand cautiously with frequent shaking, the sand may be largely introduced into the bottle of shot. About 500 liters of hydrogen chloride gas may be passed into a liter of ice water with comparatively little increase in volume, and of ammonia,

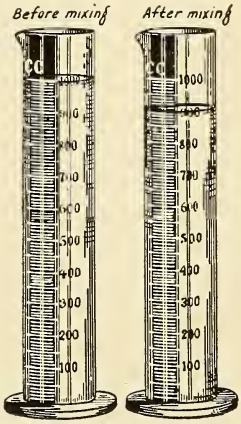



Fig. 24.—Contraction of volume on mixing two liquids.

more than 1,000 may be thus introduced. Experiments with solids many years ago showed that they were porous. Metal globes filled with water were subjected to pressure and were flattened. The liquid was forced through the metal and, appearing as drops upon the outside, showed that there were spaces between the particles of the solid through which the water particles could pass. Another experiment made some years ago in London proves not only the same thing, but that the par-

ticles of a solid are even free to move about from one place to another. Some cylinders of lead were placed upon sheets of gold and allowed to remain thus for four years. Analyses were then made of the lower end of the lead cylinders and the gold was found to have penetrated them to a distance of 8 mm.

10. **Molecular Theory.**—The foregoing and many other experiments have led scientists to believe as conclusive that matter is not continuous, but made up of minute particles not touching each other. To these they have given the name of *molecules*. They are the smallest division of matter possible without destroying the identity of the substance. Thus a molecule of water or of salt would possess all the essential characteristics of the larger mass of water or salt. In solids these molecules are close together; in liquids farther apart, and in gases at relatively very great distances. To illustrate: In a gas under ordinary room conditions, the individual molecules are relatively farther apart than is the moon from the earth, when diameters are considered. The diameter of the earth is about 8,000 miles, so that the distance of the moon is only about 30 times the diameter of the earth. Many gases may be compressed thirtyfold and still remain gases, showing that their molecules are still far apart. A gas which may be compressed by ten thousand atmospheres would have its molecules brought ten thousand times nearer together than they were; ten thousand times the diameter of the earth would approach in distance that of the sun from the earth. This gives some idea of the real distance of the molecules from each other. A bottle *full* of hydrogen, as we say, is really a bottle with comparatively few particles of the gas at relatively great distances from each other. It is difficult for the human mind to form any conception of the infinitesimal size of

a molecule. Someone has said that if a buckshot were magnified to the size of the earth and the composing molecules likewise were magnified, they would then be something like the size of the buckshot. Lord Kelvin, the great English scientist, has shown that in solids, the distance from the center of one molecule to the center of the next is not less than one five-hundred-millionth of an inch. So if they were actually touching, their diameters would be one five-hundred-millionth of an inch. If their distances apart equal the diameter of the molecule, then their diameters would be one half as great or one billionth of an inch. To count the number possible of lying upon a line 1 inch long, at the rate of one per second, would require nearly 39 years of 360 days each, ten hours per day. Automobiles, equal in number, with a wheel-base of 120 inches spaced 10 feet apart would form a procession reaching a little more than seventy-five times around the earth.

11. **Molecules Not at Rest.**—At several times in preceding chapters it has been necessary to refer to the fact that the particles of gases or liquids are not at rest. The experiment of Roberts-Austin of the gold leaf under the lead cylinders shows the same for solids. Molecules are not like dust particles in the air. These soon settle when the existing cause is removed, but not so with molecules. According to Boyle's law, when the pressure is removed from gases, they tend to expand indefinitely, so that a pint of any gas opened into a vacuum, no matter how large, would be quickly distributed throughout the entire space. The passage of a gas throughout the space occupied by another or of one liquid through another has been spoken of as *diffusion*, and can be explained only on the assumption that molecules possess the inherent power of motion and that they are continuously

in motion. This is known as the *kinetic* theory of gases.

12. **Gas Pressure, Result of This Motion.**—By methods not necessary to be discussed here, it has been learned that the average velocity with which these gas molecules are moving is very considerable. With the lightest gases such as hydrogen, it is several miles per second. Naturally, therefore, the numerous successive impacts upon the wall of any containing vessel must produce a pressure. Such is the cause of the pressure exerted by any gas upon the inside of the containing vessel and is simply its resistance to being compressed. It is not the same as the air pressure upon a surface at any particular altitude, for that is merely the weight of the column of air supported at that point. In discussing hydrates in Chapter II, it will be remembered that a manometer tube was mentioned as being used to show the pressure of the water vapor at different temperatures. It is simply the impacts of the molecules of vapor upon the surface of the mercury that push it up into the bent tube. Similarly, when we pump air into an automobile tire and the pressure gauge registers an increase from 40 to 80 pounds, we have simply doubled the quantity of air in the tire so that the number of impacts per second has been doubled.

13. **The Atomic Theory.**—John Dalton, a scientist who died in 1844, showed conclusively that while the assumption of the molecular structure of matter satisfies most of the needs of physical phenomena, it does not explain many things in chemistry. He proposed what is now known as the atomic theory. The most important features of this theory are, first, that molecules are capable of division into still smaller particles, which he called *atoms*. The word means *not able to be divided*, and up to comparatively recent years the atom has been

regarded as the smallest possible division of matter. It is usually defined as the smallest particle of matter capable of entering into a chemical reaction. Second, it is as-

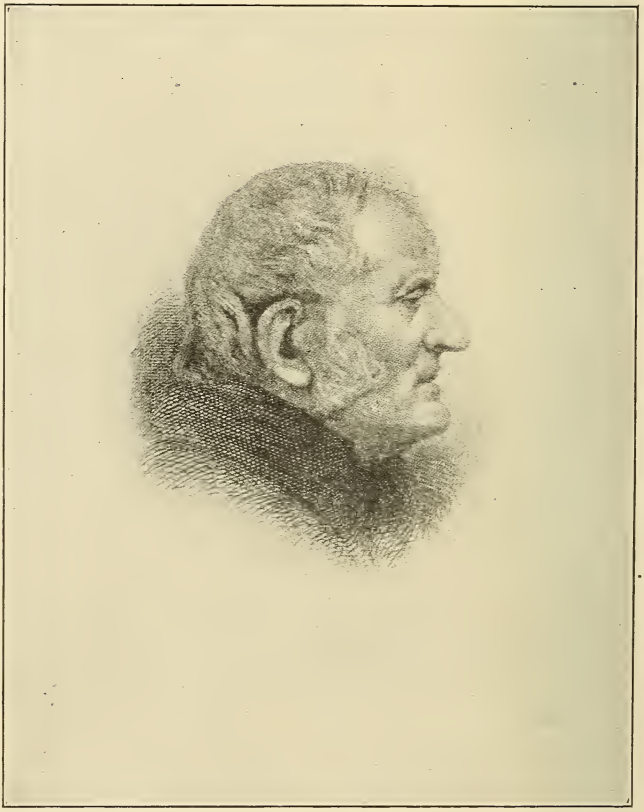


Fig. 25.—Dalton, who proposed the atomic theory of matter.

sumed by this theory that the atoms of each particular element have a definite and fixed weight. Hence, when they enter into combination, one or more of these definite weights must be used. Third, the weight of an atom

of each element is different from that of every other element; fourth, chemical action takes place between atoms and not between larger masses. Accordingly, to use a somewhat unscientific illustration, matter is tied up by nature in small packages or bundles, and when these are used together in chemical reactions it becomes necessary to use one, two or more of the packages.

14. **The Corpuscular Theory.**—As stated just above, the word atom means unable to be divided. Recently, however, it has been found that certain substances, radium for example, are able to give off particles with a velocity nearly the same as that of light and with a mass about one-thousandth part that of the hydrogen atom. These particles are called *electrons* or *corpuscles*, and are found to carry a negative charge of electricity. Further, electrons, no matter what their origin, all seem to be of the same mass. Prof. J. J. Thompson suggests that just as the molecules of a gas are at great distances from each other, so are these electrons in the atom, and he compares them to a thousand dots (.) scattered throughout a church building. The work of Thompson and of other experimenters seems to admit of no doubt as to the truth of the theory, yet it in no way lessens the value or destroys the probability of the truth of the atomic theory. Chemical action is between or among atoms, and the existence of electrons simply aids in explaining many phenomena observed which otherwise is not possible.

15. **Atomic Weights.**—It was stated above that Dalton's atomic theory assumes that the atoms of each element have a particular and definite weight. Naturally, it will be understood that to weigh anything so small as an atom is impossible. Hence, atomic weights are merely relative weights. As hydrogen is the lightest of all substances, it would be presumed that its atom would be

used as a standard for measuring others. This was at first done and the term *microcrith* was applied to the unit. On this basis the weight of the oxygen atom is approximately 16, more accurately, 15.998. It was found, further, that if the hydrogen atom was assumed to have a weight of one microcrith, the atomic weights of a large number of other elements differ considerably from *whole numbers*. On the other hand, if oxygen is assumed as weighing exactly 16 microcriths, which will give hydrogen a weight of 1.008, a very considerable number of the other elements will have atomic weights of either whole numbers or closely approaching these. On account of the advantage which this affords in accurate chemical calculations, it is regarded as preferable. Tables of atomic weights are, therefore, usually given on the basis of the oxygen atom having a mass of 16 microcriths. To define atomic weight, therefore, we would say that it is the weight in microcriths of an atom of any element as compared with the oxygen atom whose mass is 16 microcriths, or with hydrogen, 1.008 microcriths. Thus when we say sulphur has an atomic weight of 32, we mean in the form of vapor it is twice as heavy as oxygen or nearly 32 times as heavy as hydrogen. (See page 441.)

16. **Molecular Weights.**—The molecular weight of a substance is the sum of the weights of all the atoms found in a molecule of that particular substance. It will be shown later that a molecule of water contains two atoms of hydrogen and 1 of oxygen. Adding the weights of two atoms of hydrogen and 1 of oxygen, gives for water a molecule weight of 18. Thus, knowing the composition of the molecule of any substance, we may determine its molecular weight.

17. **Avogadro's Hypothesis.**—The great Italian physicist in 1811 formulated the hypothesis which bears

his name. It is, *Equal volumes of all gases under the same pressure and temperature, contain the same number of molecules.* To illustrate, this simply means that if 1 c.c. of hydrogen contain a thousand molecules, one of oxygen or any other gas would contain the same. No absolute experimental proof of its truth has been furnished, but similar changes of volume for all gases under varying temperatures and pressure, as well as many other ob-

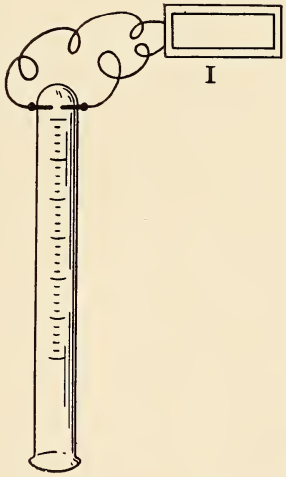



Fig. 26.—A simple eudiometer connected to induction coil, marked I.

served facts, are strong presumptive evidences of its truth.

18. **Numbers of Atoms in a Molecule.**—Assuming the truth of the hypothesis just given, it is possible to ascertain the number of atoms in a molecule of the various gaseous elements or of those which may be vaporized. For example, it has been found that water consists of two volumes of hydrogen to one of oxygen. If the converse of the experiment described in Chapter II be car-

ried out with an apparatus called a *eudiometer,* shown in Fig. 26, and correction be made for temperature, this fact is observed:

2 volumes of hydrogen exploded with 1 of oxygen produce 2 volumes of steam, or putting it more concretely,
20 c.c. hydrogen with 10 c.c. oxygen produce 20 c.c. steam.

The experiment shows that the 30 c.c. of mixed gases when combined yield only 20 c.c. of the vapor, there being a condensation of one-third. Applying Avogadro's hypothesis, supposing there are 20 thousand molecules in the 20 c.c. of hydrogen, and substituting we should have—

20 thousand mol. hydrogen with 10 thousand mol. O. produce 20 thousand mol. steam;
or,
2 mol. hydrogen + 1 mol. oxygen give 2 mol. steam.

Now it must be admitted as true that each molecule of steam contains some oxygen; hence, as there are 2 molecules of steam produced for every molecule of oxygen, the oxygen molecule must have been divided into two parts. Using the same apparatus and substituting chlorine for oxygen, but using equal volumes of each gas, the experiment may be repeated, with these results:

20 c.c. hydrogen + 20 c.c. chlorine give 40 c.c. hydrogen chloride.

Here it will be noticed that although chemical change has taken place the volume has not changed, the new substance having the same as the combined volume of the mixed gases. Applying Avogadro's hypothesis as before,

2 mol. hydrogen + 2 mol. chlorine give 4 mol. hydrogen chloride.

Now since the number of hydrogen chloride molecules is double that of the hydrogen molecules, each one of

the latter must have been broken into at least two portions. Likewise has the chlorine molecule. Since no cases have ever been observed in which the molecules of these gases are broken into more than two parts, it is assumed that a smaller division is impossible chemically and these particles are atoms. With the exception of ozone, which has been stated as being a peculiar form of oxygen, with three atoms to the molecule, all the *common* elementary gases, like hydrogen and chlorine, have two atoms to the molecule and are said to be *diatomic.* Argon, helium, and the other rare gases, belonging to the same family, are *monatomic.* Mercury and some other metals are likewise monatomic, while phosphorus and arsenic are tetratomic.

19. **Gay-Lussac's Law.**—In all the experiments outlined just above where one gas combined with another, it will be noticed that the volumes always bore some simple relation to each other. When weights are considered, this is often not true. For example, in common salt by weight chlorine unites with sodium in the proportion of about 35.5 to 23. In volumes it will be seen that *exactly* two of hydrogen combine with one of oxygen to form water; one of hydrogen combines with one of chlorine to produce hydrogen chloride, and three of hydrogen with one of nitrogen to form ammonia. This has been discovered to be a general truth and has been formulated in what is known as Gay-Lussac's law. It is usually stated thus: *The volumes of gases when uniting with each other chemically and of the gaseous products formed by the union may always be expressed in small whole numbers.* This law will be further illustrated in the following chapter in some problems of combustion.

20. **Determination of Molecular Weights.**—It has been found by experiment that a liter of hydrogen weighs

.0898 grams, and one of oxygen 1.429; or, in larger amounts, 22.4 liters of hydrogen weigh 2 grams and the same volume of oxygen, 32 grams. According to Avogadro's hypothesis, since there are the same number of molecules of each gas in the 22.4 liters, the relative weight of the two must be the *relative* weight of the two molecules. It may be said, in fact, that 22.4 liters of *any gas* will always weigh approximately as many grams as there are microcriths in the molecular weight of that gas. It has been stated above that hydrogen and oxygen are both diatomic gases; hence, since their atomic weights are 1 to 16 respectively, their molecular weights would be 2 and 32 respectively which correspond to the weights in grams given above for 22.4 liters. Likewise, the molecular weight of carbon monoxide is 28, and 22.4 liters weigh approximately 28 grams. This fact may be used to determine the molecular weight of various gases. For example, 22.4 liters of carbon dioxide weigh approximately 44 grams; hence, the molecular weight of this gas would be 44.

21. **Gram Molecular Weight.**—The molecular weight of any substance, stated in grams, is called its *gram molecular weight*. Thus the molecular weight of water is 18; of cane sugar, 342; hence, 18 grams and 342 grams would be respectively gram molecular weights of these two substances. Sometimes such a weight is spoken of as a *mol* or a *molar weight*. If a gram molecular weight of various gases be measured under standard temperature and pressure, allowing for slight variations which admit of explanation, the volume is always approximately 22.4 liters. Thus,

Hydrogen, 2 grams occupy 22.4 liters
Oxygen, 32 grams occupy 22.4 liters
Nitrogen, 28 grams occupy 22.4 liters
Carbon Dioxide, 44 grams occupy 22.4 liters

Conversely, therefore, if we determine the weight of 22.4 liters of any gas we have a means of knowing approximately its molecular weight. This method often serves in checking up other methods of finding molecular weights and in this way is of great value.

### Exercises for Review

1. Name the three states of matter and the two forces which govern them.

2. State Charles' law. Illustrate. What is the absolute zero point? How did it come to be adopted?

3. State Boyle's law. What is meant by standard pressure and temperature?

4. What is the formula for correcting volumes when both temperature and pressure change?

5. What is meant by aqueous tension? Would it be used when a gas is collected over mercury? Explain.

6. What can be said about the contiguity of matter? Why must this conclusion be reached?

7. Give some experimental proof that matter is not continuous.

8. What is the molecular theory? A molecule? Give some idea of the size of a molecule; of the distance they are apart in gases.

9. What proofs can you offer that molecules are not at rest?

10. What gives the pressure on the inside of a tire on a motor car? If you double the quantity of air already in a tire what effect upon the pressure? Why?

11. Give the four main assumptions of the atomic theory. What is an atom?

12. What is an electron? What can you say of its mass? Does this theory destroy the truth of the atomic? Why?

13. What is meant by the atomic weight of an element? Illustrate. What is a microcrith?

14. State Avogadro's hypothesis. Of what use is it?

15. What is a monatomic molecule? A diatomic? Name some.

16. Give one method of determining experimentally the molecular weight of a gas.

## CHAPTER VII

## SYMBOLS AND FORMULAS

**Outline—**

The Origin of Symbols
Present Use of Symbols
Formulas
  (*a*) Empirical
  (*b*) Structural
Radicals
Equations

1. **Origin of Symbols.**—The use of symbols began with the alchemists who sought thereby to render unintelligible the notation of their attempts at making gold from the baser elements. Modern chemists have found it necessary in mathematical calculations and in various other ways to use short methods of representing chemical compounds and the reactions taking place. Moreover, chemical symbols as now used are intelligible to all chemists the world over, so that out of a plan adopted to keep secret the work done has come a universal language read by all chemists.

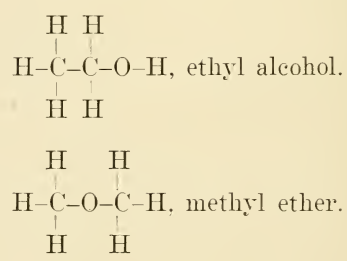
2. **What Are Symbols?**—A symbol is a letter or letters used to represent a *single atom* of an element. Usually it is the initial letter, but as this is the same for a number of elements, the initial letter is often followed by some other distinctive one of the word. It must be noted that the initial letter is always capitalized, while the second, if another be used, is not. Thus C is the symbol for carbon; Ca for calcium; Cd for cadmium; Co for cobalt. Several of the elements receive their symbols from the Latin or some other foreign language; thus, K is for

potassium, *Kalium;* Na for sodium, *Natrium;* Ag, silver, *Argentum;* Hg for Mercury, *Hydrargyrum.*

3. **Formulas.**—A formula is a combination of symbols representing a *molecule* of a substance, usually that of a compound. In its broadest sense it may represent the molecule of an element. Thus, HCl is the formula for hydrogen chloride, while HH, usually written $H_2$ is the formula for a molecule of hydrogen. To represent the formula of a compound naturally the number of atoms of each element contained must be shown. If there be more than one of any of them, that fact is indicated by a small figure written at the right and slightly below the symbol to be multiplied. Thus, water is $H_2O$, showing two atoms of hydrogen to one of oxygen per molecule: likewise sulphuric acid has the formula, $H_2SO_4$; sugar, $C_{12}H_{22}O_{11}$. Sometimes a certain group or combination of symbols will be contained more than once in the compound; in such cases the group is usually enclosed in parentheses and the number of times it is contained expressed by a subfigure. Thus, aluminum carbonate is $Al_2(CO_3)_3$ in which the group $CO_3$ occurs three times. It might be written $C_3O_9$, but for reasons which will appear later the method first given is usually followed. If it is desired to represent more than a molecule of a substance, the proper figure is placed before the formula as a coefficient. Thus, $5K_2CO_3$ indicates five molecules of potassium carbonate and the coefficient multiplies each symbol in the formula. That is, in $5K_2CO_3$ there are not only ten atoms of potassium, but five of carbon and fifteen of oxygen. Sal soda has the formula, $Na_2CO_3.10H_2O$. Written thus it is typical of the method used for all hydrates. The number of molecules of water entering into the compound is indicated by the coefficient of the water. Written thus, that the compound is a hydrate, is indicated

at once, as is also the fact that the combination is somewhat of a molecular or loose one.

4. **Structural Formulas.**—Often it is very desirable to show how the atoms are arranged in the molecule. Especially is this true in the case of many compounds of carbon, in which two or more may have the same percentage composition and same molecular weight, but very different properties. Thus, $C_2H_6O$ is the *empirical* formula for more than one compound in which there are two atoms of carbon, six of hydrogen and one of oxygen per molecule, but the formula shows nothing more. Obviously, if written $C_2H_5OH$ or $(CH_3)_2O$, the molecular weights are the same, but the first indicates an alcohol and the second an ether. To the chemist, written thus, they indicate the manner of arrangement of the atoms in the molecule. This is shown more fully thus:




Such formulas as these are called *structural* or sometimes *graphic*, and in very complex compounds are of the greatest help in understanding the relations existing.

5. **Radicals.**—In many compounds certain groups of elements will be found, which behave as if they were single elements. Thus in sulphuric acid and in all the sulphates there occurs the group, $-SO_4$. This constitutes the negative portion of the compound and in case of electrolysis appears at the positive electrode. It can-

not be separated out or isolated, and in the electrolytic apparatus it immediately combines with the anode if that be possible; if not, it combines with hydrogen from the water present and forms a molecule of sulphuric acid. Looking at the formulas, $K_2SO_4$, $CuSO_4$, $Al_2(SO_4)_3$, $K_2Al_2(SO_4)_4$, we see the same combination of elements. All such groups are called *radicals*. Ordinarily the term indicates a group of atoms forming a *part* of a compound but unable to exist alone. There is only one common electropositive radical, ammonium, $NH_4$-; it is found in all ammonium compounds. Thus ammonium chloride, $NH_4Cl$, ammonium sulphate $(NH_4)_2SO_4$. The other more common radicals are -$NO_3$ seen in nitric acid and all nitrates, -$CO_3$ in the carbonates, -$PO_4$ in phosphates, -$ClO_3$ in chlorates, -HO in hydroxides.

6. **Equations.**—Chemical changes or reactions have been classified as being mainly of three kinds. It is customary among chemists to show what takes place in a chemical change by an equation. The left hand side contains the formulas of the substances used and the right hand side, the products formed, with the sign $\rightarrow$ between, which is read *yields* or *produces*. Going back to the experiment of heating mercuric oxide, we find that,

Mercuric oxide, heated, yields oxygen and mercury. For the sake of brevity this is written,

$$HgO \text{ (heated)} \rightarrow Hg + O$$

or better,

$$2HgO(\text{heated}) \rightarrow 2Hg + O_2.$$

It was stated in the preceding chapter that the oxygen molecule contains two atoms. It is known that all substances exist as aggregations of molecules and not of atoms. The second equation just above shows the oxy-

gen in the molecular form as it would exist after it has been liberated from the compound, hence is the better form.

Again, water electrolyzed, gives hydrogen, two parts and oxygen, one. More briefly, but indicating the same thing,

$$2H_2O \rightarrow 2H_2 + O_2$$

Equations are not something merely abstract as equations in algebra, or merely theoretical. Every equation must be verified by actual experiment, otherwise it has no value. For example, we prepared hydrogen by allowing sodium to react with water. Algebraically we might write the equation,

$$2Na + H_2O \rightarrow Na_2O + H_2 \text{ or}$$
$$2Na + 2H_2O \rightarrow 2NaHO + H_2.$$

Only by experiment can we know which is correct. The first of the two equations shows sodium oxide formed; the second, sodium hydroxide. Which is correct? Chemical tests show that, performed as the experiment was, sodium hydroxide is present; hence, the equation must be written to show that fact. We prepared oxygen by heating potassium chlorate, $KClO_3$. Theoretically, all or part of the oxygen might be displaced by heating the compound, just as was the case when sodium reacted, as above, with water in producing hydrogen. Testing the residue shows that potassium *chloride* is present, and our equation must be written to indicate the fact, thus,

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

In like manner all equations are determined by experiment and merely state in brief form what was learned thereby.

### Exercises for Review

1. What was the origin of symbols? Give the purpose of a symbol now.

2. Define a symbol.

3. Of what do symbols consist and how written? Illustrate.

4. Give several derived from the Latin or Greek.

5. What is a formula and what does it represent in its broadest sense?

6. What effect has a coefficient before a formula? Illustrate. How is it different from the coefficient as used in algebra?

7. What is a structural formula? Of what advantage?

8. What is a radical? Give five. How are they different from compounds?

9. What is the purpose of an equation? What do they show?

10. Which is the better form, and why: $2K + 2H_2O \longrightarrow H_2 + 2KHO$, or, $K + H_2O \longrightarrow H + KHO$?

11. How do chemists know whether an equation is correct?

12. Is this equation true: $CuSO_4 + 2KHO \longrightarrow Cu(HO)_2 + K_2SO_4$? How can you find out?

## CHAPTER VIII

## SOME CHEMICAL PROBLEMS

Outline—

- Practical Value of the Equation
  - Problems in Manufacturing Industries
- Percentage Composition of Compounds
- Problems in Combustion
- Liter Weights of Gases
- Determination of Formulas

**1. Value of Equations.**—Almost every manufacturing industry involves more or less chemistry. In baking powders, of the three ingredients most often used, two of them must be exactly proportioned, otherwise the food in which they are used will be valueless. The chemical change occurring when such chemicals are put together is first determined by experiment in the laboratory; this is then expressed by an equation, and from this without repeating the experiment the quantities needed may be calculated by any one at any time. To illustrate with a case somewhat simpler than that of baking powder, we have learned that

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

This equation shows that two molecular weights of potassium chlorate produce three molecular weights of oxygen. Calculating these weights from the table of atomic weights given on p. 441, we find that 245 parts of potassium chlorate yield 96 of oxygen. Suppose a manufacturer needs to know how much oxygen he can obtain from 1,000 grams of potassium chlorate. Knowing from

the equation that 245 grams of the chlorate will produce 96 of oxygen 1,000 will produce $x$ grams, or

$$245 : 96 :: 1{,}000 : x,$$

from which $x$ may be easily calculated. Or, putting it in another form, the oxygen obtained is seen to be 96/245 of the weight of the chlorate used. The oxygen obtained, therefore, would be

$$96/245 \text{ of } 1{,}000 = \frac{96 \times 1{,}000}{245}$$

Manufacturers of oxygen for use in the oxyhydrogen blowpipe or for other purposes furnish it in gaseous form, which might sometimes be given in volume and not weight as above. Knowing the weight of a liter of oxygen, 1.43 gram, which may be obtained by multiplying the weight of a liter of hydrogen by the density of oxygen, if we divide the weight obtained above by the weight of a liter of oxygen we shall have the volume. It may also be obtained another way, which is often easier. It has already been stated that a gram molecular weight of oxygen as of any other gas is 22.4 liters. By looking at the equation,

$$2KClO_3 \rightarrow 2KCl + 3O_2,$$

we see that two molecular weights of potassium chlorate produce three molecular weights of oxygen. But 3 gram molecular weights of oxygen would be, in volume, three times 22.4 liters. That is, 245 grams of potassium chlorate would produce $3 \times 22.4$ liters of oxygen, or 67.2 liters. Hence, 1,000 grams of potassium chlorate would yield

$$\frac{1{,}000}{245} \times 67.21.$$

This would be the volume under standard conditions of

temperature and pressure. If the gas is to be delivered under five atmospheres' pressure, according to Boyle's law, five volumes of the uncompressed gas must be prepared for every one of that to be delivered.

2. **To Find Percentage Composition.**—Knowing the formula, the method is very simple. Suppose it is desired to know the amount of water contained in Epsom salt, $MgSO_4.7H_2O$. Ascertaining the atomic weights from the table, p. 441, we have

$$24 + 32 + 64 + (7 \times 18) = 246.$$

The weight of the seven molecules of water is 126. It is, therefore, 126/246 of the whole compound, or 51.2 per cent.

3. **Some Combustion Problems.**—Ordinary combustion has been defined as rapid oxidation. It is often desirable to know the character and quantity of products formed as well as the amount of air needed for perfect combustion. Natural gas consists mainly of what is known as marsh gas, $CH_4$. When it burns the following equation illustrates the change taking place,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

This shows that one volume of marsh gas requires two volumes of oxygen and produces one of carbon dioxide and two of vapor. Applying Avogadro's hypothesis, any problems involving volumes may be *read off* at once from the equation. Suppose 1,000 cubic feet of marsh gas are burned; from the equation we can see that twice as much oxygen would be needed and there would be produced the same volume of carbon dioxide and twice the volume of water vapor. As air is only about one-fifth oxygen, to burn this volume of gas would require

10,000 cubic feet of air. Acetylene is a gas producing great heat when properly burned and often used in blow pipe work for welding,

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O.$$

The equation indicates that two volumes of acetylene require five of oxygen and yield four of carbon dioxide and two of vapor. From this it is seen at once that 1,000 cubic feet of the gas would need two and a half times as much oxygen or 2,500 cubic feet, and would produce 2,000 cubic feet of carbon dioxide and 1,000 of vapor. When rooms are warmed by an open gas heater or by an oil stove, by which the necessary oxygen is taken directly from the room and the products left in the room, it is seen how rapidly the air is being vitiated. The water produced in such cases is often sufficient to loosen the paper upon the walls, and even the parts of furniture glued together. It must be remembered that the air being used is more than five times the volume of the oxygen shown in the equation.

4. **To Find the Weight of a Liter of Any Gas.**—It is not necessary for the student to commit to memory many figures. But the weight of a liter of hydrogen should be remembered, for by means of it the weight of a liter of other gases may readily be calculated. It is necessary first to determine the *vapor density* of the gas, that is, its density compared to hydrogen. Obviously, from Avogadro's hypothesis, if we divide the molecular weight of any gas by the molecular weight of hydrogen, we shall have the density of the gas compared to hydrogen. The molecular weight of hydrogen is 2, hence dividing the molecular weight of any gas by 2 gives its vapor density. Then, knowing the weight of a liter of hydrogen, if we multiply this by the density we shall have the

weight of a liter of the gas in question. To illustrate: Take carbon dioxide, $CO_2$. It has a molecular weight of 44; its vapor density would, therefore, be 22: multiplying the weight of a liter of hydrogen, .0898, by 22 gives 1.9756 as the weight of a liter of carbon dioxide.

5. **Determination of Formulas.**—Knowing by experiment the percentage composition of a substance, and the atomic weights of the elements contained, it is possible to determine the empirical formula. Thus, wood alcohol contains 37½ per cent of carbon, 12½ per cent of hydrogen and 50 per cent of oxygen. Dividing these percentages by the atomic weight of each element, on the assumption that they are microcriths of weight and not percentages, we have

$$\frac{37.5}{12} = 3.125 \qquad \frac{12.5}{1} = 12.5 \qquad \frac{50}{16} = 3.125.$$

Had the figures representing per cents really been microcriths, as assumed, the quotients would have been the number of atoms of each element in the formula. While the assumption is not true, the mathematical relation obtained is true, that is, for every 3.125 atomic weights of carbon there would be 12.5 atomic weights of hydrogen and 3.125 of oxygen. If we divide through by the smallest of these weights we shall remove the fractional amounts and obtain as a result, carbon, 1; hydrogen, 4 and oxygen, 1. The formula, therefore, would be $CH_4O$. To know whether this is correct the vapor density of the alcohol must be determined. Suppose by experiment this is found to be 16. We know from a previous statement that the molecular weight is double the density, hence the molecular weight of this compound would be 32. By adding the atomic weights represented in the formula obtained, $CH_4O$,

we obtain 32, which agrees with the weight obtained by experiment; hence is correct. Take another case. Analysis of sulphuric acid shows it to contain hydrogen, 2.04 per cent; sulphur, 32.65; oxygen, 65.30. Dividing these figures by the respective atomic weights we have as the quotients, 2.04, 1.02 and 4.08, which give the *relative* number of atomic weights contained in the molecule. Dividing by the smallest quotient, we have as a result, 2, 1, 4 respectively, giving for the formula $H_2SO_4$. Again, acetylene has a percentage composition of carbon, 92.31, and hydrogen, 7.69 per cent. Dividing by the atomic weights we have as the quotients, 7.7 and 7.69. Dividing these results by 7.69 we have 1 and 1 respectively, which gives as the empirical formula for acetylene, CH. Is this correct? By experiment in the laboratory a liter of acetylene is found to weight 1.167 grams. As a liter of hydrogen weighs .0898 grams, acetylene is found to be thirteen times as heavy. The molecular weight, therefore, must be $2 \times 13$, or 26. If CH were the formula, its molecular weight would be only 13; hence, the empirical formula we obtained by calculation is just half the correct one; in other words, it must be doubled, so that it becomes. $C_2H_2$.

**Exercises for Review**

1. Determine the weight of oxygen obtainable from 980 grams of potassium chlorate. What volume would the oxygen have?

2. How much potassium chlorate would be needed to prepare 500 liters of oxygen if under five atmospheres' pressure?

3. What weight of hydrogen may be had from 260 grams of zinc by allowing it to react with sulphuric acid? Suppose hydrochloric acid were used, what would be the weight of hydrogen?

4. What weight of sulphuric acid would be needed to react with 100 grams of magnesium in preparing hydrogen? What would be the volume of the hydrogen obtained?

5. Calculate the per cent of sulphur in sulphuric acid. Also the per cent of oxygen.

6. What is the percentage of water in sal soda; formula, $Na_2CO_3 10H_2O$?

7. The gas ethylene has the formula, $C_2H_4$. If 1,000 liters of it are burned, what volume of carbon dioxide is produced and what of water vapor?

8. Find the weight of a liter of oxygen; of carbon monoxide, CO; of ozone; of nitrogen monoxide, $N_2O$; of arsenic vapor.

9. The percentage composition of a certain alcohol is carbon, 52.17, hydrogen, 13.04, and oxygen 34.78. Find the empirical formula.

10. If the vapor density of nitric oxide is 15, is its formula NO or $N_2O_2$?

# CHAPTER IX

## THE HALOGENS

**Outline—**

- Relation of the Halogens to Each Other
- Chlorine, its History
  - (*a*) Preparation in Laboratory
  - (*b*) Commercial Methods
  - (*c*) Physical Characteristics
  - (*d*) Chemical Characteristics
  - (*e*) Uses
- Hydrogen Chloride
  - Characteristics
- Hydrochloric Acid
  - (*a*) Preparation
  - (*b*) Characteristics
  - (*c*) Uses
- Hydrofluoric Acid
  - Uses
- Bromine
  - (*a*) Occurrence
  - (*b*) Preparation
  - (*c*) Characteristics
  - (*d*) Uses
- Iodine
  - (*a*) Occurrence
  - (*b*) Preparation
  - (*c*) Characteristics
  - (*d*) Uses

1. **General View.**—There are four elements in the halogen group—fluorine, chlorine, bromine and iodine. They are called *halogens,* a word meaning *salt producers,* because they all produce many compounds resembling common salt; and from the similarity of their physical characteristics and their chemical behavior, must be regarded as belonging to a single group of elements. Their

densities compared to hydrogen are in the order given above, with atomic weights, respectively of, approximately, 19, 35.5, 80 and 127. Their chemical activity is in the inverse order of their densities, that of iodine being the least. All have an irritating odor, although that of iodine is rather feeble when compared with the others. The two lightest are gases; bromine is a liquid, the only liquid element except mercury, and iodine is a solid.

2. **Discovery of Chlorine.**—It will be remembered that in 1773 Scheele prepared oxygen by heating manganese dioxide with sulphuric acid. The following year he obtained chlorine by treating manganese dioxide with hydrochloric acid, although he had no idea he had discovered a new element. Knowing that it was possible to obtain oxygen from manganese dioxide, he believed he had simply caused a union between the hydrochloric acid and the oxygen of the dioxide. And, in accordance with the phlogistic ideas of combustion, he named the gas *dephlogisticated marine acid air.* At that time oxygen was often called dephlogisticated air; hence, the name in modern chemical terms would be oxidized hydrochloric acid gas, for *marine acid* was then what we now call hydrochloric. More than a quarter of a century passed away and chlorine was still unknown as an element until Sir Humphrey Davy gave it a careful study and so pronounced it.

3. **Preparation of Chlorine.**—The usual laboratory method of preparing chlorine is the same as used by Scheele. (Fig. 27.) The accompanying figure shows one form of apparatus and the method of collecting. Being a gas much heavier than air it may be collected by *downward displacement.* As it is considerably soluble in water, the plan used in the case of hydrogen and oxygen is not satis-

factory, but may be employed if the water has a considerable amount of common salt dissolved in it. The manganese dioxide is placed in the flask, and when the collecting bottles are all ready the hydrochloric acid is added through the thistle tube and gentle heat applied as needed.

4. **Commercial Methods.**—As chlorine is used so extensively in various ways, several processes of obtaining it cheaply have been devised. Since common salt is

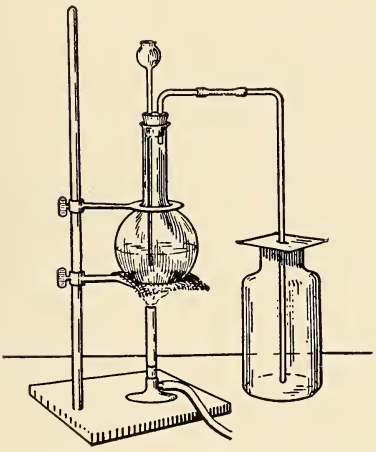


Fig. 27.—Preparation of chlorine in the laboratory.

abundant and not expensive, one of the plans widely adopted is that of separating its constituents, sodium and chlorine, by electrolysis. There are many difficulties in the way of carrying out the method successfully, but one type of machine is shown in Fig. 28. In the center compartment the bundle of carbon rods serves as the cathode, while a heavy carbon rod enters each of the two outer compartments, giving a double anode. The cathode dips into pure water, the anodes into sat-

urated salt solution; a thin layer of mercury covers the bottom of the apparatus and fills two grooves into which the partitions dip, shown by the heavily shaded portion in the figure. Chlorine being an electronegative element is liberated at the anodes and is drawn off, dried, and compressed in tanks or drums. The sodium, electropositive, is repelled by the anodes, moves toward the cathode, meets the mercury and is dissolved by it. In the figure, E is an eccentric which rocks the tank continually. In this way the mercury containing the sodium is brought into contact with the water, where-

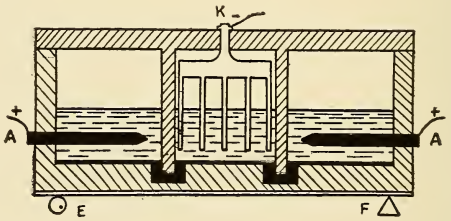



Fig. 28.—Manufacture of chlorine.

upon the sodium reacts with the water forming sodium hydroxide. The two reactions are

$$2NaCl \rightarrow Cl_2 + 2Na,$$
$$2Na + 2H_2O \rightarrow H_2 + 2NaHO.$$

5. **Physical Characteristics of Chlorine.**—Chlorine is a greenish-yellow gas, about two and a half times as heavy as air, and of very irritating odor. It may be liquefied at −33.6° C. at atmospheric pressure and in this condition is a limpid, golden yellow fluid. It may be kept thus sealed hermetically in strong glass tubes. At about −102° C. it becomes a pale yellow solid, which upon further cooling changes to a pure white substance resembling snow. Upon melting it assumes the same

yellow color again. It is soluble in water about two volumes to one.

6. **Chemical Characteristics.**—Chlorine is an exceedingly active element, possibly even more so than oxygen. Nearly all the metals, especially in a finely divided form or in thin sheets, ignite spontaneously in chlorine. Sodium must be heated before combustion takes place, but when this is done the action is vigorous with the formation of common salt. Turpentine, near its boiling point, on a strip of blotting paper, when lowered into a jar of chlorine, catches fire almost instantly, producing an immense quantity of black smoke. Yellow phosphorus in a deflagrating spoon in chlorine begins to burn almost immediately, and a jet of hydrogen, lighted in the air, continues to burn as well or better than before. From these experiments it is evident that combustion means more than the union of a substance with oxygen. *Any two substances,* combining with such rapidity as to produce heat and light, undergo combustion. Chlorine attacks the throat and bronchial tubes, causing great suffering for which there is no good antidote. A saturated solution of chlorine in water, if surrounded by ice, deposits yellow crystals of chlorine hydrate, having the composition $Cl.4H_2O$. A mixture of equal parts of hydrogen and chlorine, if exposed to bright sunlight, explodes with violence. The light from a burning magnesium ribbon will bring about the same results. A solution of chlorine in water, exposed to strong light, decomposes, forming hydrochloric acid and setting free the oxygen. This is shown by a simple experiment illustrated by Fig. 29. The test tube is filled with chlorine water and inverted over an evaporating dish partly filled with the same solution. In a short time, bubbles of gas may be seen rising to the top of the tube; when the action has

ceased the color will all have disappeared from the water. Chemical tests show that the gas is oxygen and that at the close the water contains hydrochloric acid. The final result is shown by the equation,

$$2H_2O + 2Cl_2 \rightarrow O_2 + 4HCl.$$

7. **Uses of Chlorine.**—Chlorine is used extensively for bleaching, especially cottons and linens. The cloth is drawn slowly through successive vats of bleaching powder solution and dilute hydrochloric acid. Thus the chlorine is set free and oxidizes the coloring matter. Much of the paper pulp used is bleached in the same way, and in the Middle West most of the large flour

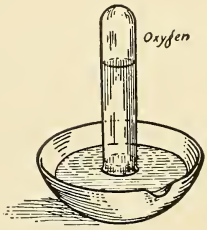



Fig. 29.—Effect of sunlight on chlorine water.

mills employ liquid chlorine to bleach their products, to enable them to compete with other flours which by nature need no such bleaching. Practically all steam laundries now use chlorine to whiten the cotton and linen goods in order to please a critical public. Such frequent use of chlorine upon the fibers of the cloth greatly weakens them and hastens the end of their usefulness. Chlorine is frequently employed as a disinfectant; its use for the destruction of pathologic germs in city waters has already been mentioned. Bleaching powder, a compound formed by the interaction of chlorine with lime is valuable in the sick-room; a small amount in a

saucer, moistened with water, slowly gives off chlorine to the air. The quantity is so small as to be unnoticeable except close at hand, yet by diffusion throughout the room brings very valuable results. Chlorine is also used in the extraction of gold from its ores: for this purpose, bleaching powder, treated with hydrochloric acid is frequently employed, but in places remote from railway or other good means of transportation liquid chlorine put up in steel cylinders is used. Chlorine was the first of the poisonous gases used in the late war. Steel cylinders filled with the gas liquefied by great pressure were opened with nozzles towards the Allies with the wind blowing in that direction. Carried down hill by its own weight and aided by the wind the huge greenish-yellow billows caused the greatest suffering and thousands of deaths. Later the gas mask was devised to protect the wearer against such attacks. In the American mask all the air taken into the lungs was compelled to pass through a specially absorptive kind of charcoal made from the shells of nuts, or of charcoal mixed with an *antichlor,* a substance which combines with the chlorine. One of the best substances of this nature is what is known by photographers under the name of *hypo* or sodium thiosulphate.

8. **Hydrogen Chloride.**—This compound has been known to chemists several hundred years, under the names, *spirit of salt* and *marine acid air.* It was so named because prepared from common salt, at that time derived mostly from the Mediterranean Sea.

9. **Physical Characteristics of Hydrogen Chloride.**—It is a colorless gas of very irritating odor, and considerably heavier than air. It is very soluble in water; a liter of water at 0° C. will absorb between 500 and 600 liters

of the gas. In other words, 600 liters are about the same as 600 quarts or three 50-gallon barrels, so that one quart of ice water will absorb about three barrels of hydrogen chloride. Blowing across the top of a tube or flask in which the gas is being evolved always shows heavy white fumes; this is because the moisture of the breath is absorbed and condensed by the gas. When a jet of hydrogen burns in a bottle of damp chlorine, or turpentine upon the blotting paper as previously described, a white cloud always appears, from the condensation of the moisture by the hydrogen chloride formed.

$$H_2 + Cl_2 \rightarrow 2HCl$$
$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C.$$

These two equations represent the burning of hydrogen and of turpentine respectively in an atmosphere of chlorine. A liter of the hydrogen chloride weighs 1.64 grams. At $-83.7°$ C. it becomes a colorless liquid and at $-110°$ a solid. The liquid has no effect upon dry metals such as zinc and others, readily acted upon by the solution of the gas.

10. **Hydrochloric Acid.**—When hydrogen chloride gas is allowed to pass into water the solution formed is called hydrochloric acid. The ordinary commercial variety, yellow in color, due to the presence of small quantities of iron chloride, is sold under the name, *muriatic acid*. It was formerly a by-product obtained in the manufacture of sodium carbonate, the first step of which involves the treatment of common salt with sulphuric acid. At temperatures such as those obtained in the laboratory with the bunsen burner, the following reaction takes place,

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4.$$

In the factories a much higher temperature is used with

double the quantity of salt which results in a different reaction, thus,

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4.$$

The gas thus obtained is conducted into towers filled with coke or some similar material, which is kept moist by water trickling over it. Owing to its great solubility the gas is all absorbed and when concentrated the solution is the acid of commerce.

11. **Characteristics of Hydrochloric Acid.**—When pure it is a colorless solution. If a weak solution be boiled it becomes more and more concentrated until it reaches about 20 per cent of hydrogen chloride; one stronger than this, if heated, gives off the gas faster than the water until it reaches a strength of about 20 per cent, when it remains constant. Ordinary concentrated hydrochloric acid contains about 36 per cent of hydrogen chloride and is strongly acid. Litmus paper is turned red as are various other vegetable colors or dyes; by such metals as magnesium, iron, zinc it is readily decomposed with the evolution of hydrogen. Thus,

$$Zn + 2HCl \rightarrow H_2 + ZnCl_2,$$
$$Mg + 2HCl \rightarrow H_2 + MgCl_2.$$

This is very different from the action of the liquid hydrogen chloride. The two are not different in appearance, but the latter, as previously stated, does not affect dry metals; neither is it a conductor of electricity, whereas the acid is.

12. **Uses.**—A century ago hydrogen chloride was a waste product of the Leblanc process of making soda crystals. Being heavier than air it settled down from the lofty towers built to carry it away, destroying vegetable life and corroding tools and everything of a me-

tallic character. When conducted into streams it killed the fish and other aquatic animals, so that eventually most stringent laws were enacted against all such manufacturers. Finally, by the aid of chemical research, valuable uses were suggested for it, and now it ranks among the most valuable of the acids. Every laboratory uses it abundantly; almost every manufacturing industry employs it to a greater or less extent. In the stomach it is believed to be an essential of digestion. The fact that bones, very imperfectly masticated, are readily digested by various carnivorous animals is explained by the excessive amount of hydrochloric acid found in their stomach, which dissolves the mineral matter from the bones and leaves them about as soft as so much gelatine. Hydrochloric acid is used mixed with nitric acid, three parts of the former to one of the latter, in what is called *aqua regia*. The words mean *royal water* and were so employed for the reason that formerly this was the only known solvent for gold, the king of metals. The solution is effected by the chlorine which is set free thus,

$$3HCl + HNO_3 \rightarrow 2H_2O + 2Cl + NOCl.$$

13. **Hydrofluoric Acid.**—The preparation of hydrogen fluoride is similar to that of the corresponding compound of chlorine. The cheapest natural compound of fluorine is calcium fluoride, known as fluor spar, $CaF_2$. This is mixed with sulphuric acid and heated in a platinum retort. A colorless, irritating gas distils over, which is caught in water. This solution is the hydrofluoric acid of commerce. It is put on the market usually in ceresine or wax bottles. At ordinary temperatures the gas is believed to have the formula $H_2F_2$. Above 30° C. it begins to decompose and at a little be-

low 90° the density of the vapor indicates a molecular weight of 20 which is that for the formula HF. Its chief use is for etching glass. The article to be etched is covered with paraffin, the design is cut in the wax so as to expose the glass, and the hydrofluoric acid is dropped on. In a very few minutes the etching is done. Graduations upon scientific instruments and apparatus such as barometers, burettes, pipettes and the like, are thus made. The following equations show the chemical reactions in preparing the hydrogen fluoride and the glass etching,

$$CaF_2 + H_2SO_4 \rightarrow H_2F_2 + CaSO_4,$$

$$CaSiO_3\ Na_2SiO_3 + 6H_2F_2 \rightarrow 2NaF + CaF_2 + 2SiF_4 + 6H_2O.$$

The silicon fluoride is a gas and escapes, while the calcium and sodium fluorides are solids which are washed away in cleaning the glass. Porcelain and chinaware, in being prepared for hand decoration, are often treated with hydrofluoric acid to remove the glazed surface and thus cause the gold or other decoration to adhere the better.

## Bromine

14. **Where Found.**—Bromine in potassium and magnesium bromide occurs in nature associated with common salt. Being more soluble than salt, these compounds do not crystallize out as readily; hence, they are usually found in the upper layers of salt beds. Our supply is largely obtained as a by-product of the salt works of Ohio, Kentucky and Michigan.

15. **Preparation.**—The method is very similar to that for the preparation of chlorine. It will be remembered that in the laboratory chlorine is made by treating manganese dioxide with hydrochloric acid. Hydrobro-

mic acid is not an article of commerce, because of its instability; hence, it must be prepared as needed. If magnesium bromide or any other bromide is treated with sulphuric acid, hydrogen bromide may be obtained, thus,

$$MgBr_2 + H_2SO_4 \rightarrow 2HBr + MgSO_4.$$

It has many properties similar to hydrogen chloride in that it is a colorless gas, has a very irritating odor, and is very soluble in water. For the last reason it condenses moisture in the air or from the breath readily. Passed into distilled water, hydrobromic acid is formed, but it very soon begins to decompose and in a few days no acid at all remains. In preparing bromine, if manganese dioxide is added to the mixture of magnesium bromide and sulphuric acid, we have conditions similar to those in the preparation of chlorine. First the hydrogen bromide is formed, then this oxidized by the manganese dioxide with the formation of free bromine. It is then distilled out and condensed under water. The following equation shows the final reaction,

$$MgBr_2 + MnO_2 + 2H_2SO_4 \rightarrow MgSO_4 + MnSO_4 + 2H_2O + Br_2$$

16. **Physical Characteristics.**—Bromine is a dark reddish-brown liquid, the only liquid nonmetallic element. It is a little more than three times as heavy as water in which it is not greatly soluble—about 3 c.c. in one hundred. It is a very volatile liquid; hence, if a bottle of it is left open it soon passes off into the air. It boils at 59° C. and solidifies at − 7.3, in slender, needle-like crystals. Its vapors are exceedingly irritating to the throat and bronchi, and upon the skin the liquid produces serious and painful burns; therefore, the utmost care must be exercised in handling it.

17. **Chemical Characteristics.**—Many of the characteristics of chlorine are observable in bromine, but in a

less marked degree. A jet of hydrogen burns in a bottle of bromine vapor producing white fumes due to the hydrogen bromide formed. A mixture of the two gases, however, is not explosive, but a platinum sponge greatly hastens the union as was the case with the chlorine and hydrogen mixture. A piece of yellow phosphorus, placed in bromine vapor, does not usually ignite, but a slow combination takes place, with the formation of phosphorous tribromide. If a small drop of liquid bromine be allowed to fall upon a piece of yellow phosphorus, the action is immediate. The chemical union is so violent that the phosphorus is ignited, bursts into fragments, and burns vigorously. Small pieces of antimony dropped upon bromine in a test tube become red-hot almost instantly, float around upon the liquid, and finally disappear. The chemical reaction is

$$2Sb + 3Br_2 \rightarrow 2SbBr_3.$$

With many other metals the action is equally violent.

18. **Uses.**—Bromine is used to some extent in the laboratory in analytical work, but more largely in the manufacture of aniline dyes. The compounds, potassium and magnesium bromide, are used in medicine, mainly as sedatives.

## Iodine

19. **Occurrence.**—Like chlorine and bromine, iodine in the form of compounds occurs in sea water. From this it is separated by certain seaweeds, especially kelp, and stored up in the form of rather complicated compounds. In many places along the Pacific Coast, notably, in the neighborhood of San Diego, vast quantities of kelp are found, so that ocean vessels are unable to make their way through. In the form of compounds, sodium iodide and iodate, iodine occurs in the saltpeter

beds of Chile as bromine does in the salt beds of the United States.

20. **Preparation.**—Formerly most of the iodine of commerce was obtained from seaweeds. They were cautiously burned so as not to vaporize the iodine present, and the ashes were treated as in the preparation of bromine, that is with manganese dioxide and sulphuric acid. The equation is similar:

$$2KI + 3H_2SO_4 + MnO_2 \rightarrow MnSO_4 + 2KHSO_4 + 2H_2O + I_2$$

The iodine distils out and is condensed. It is purified by vaporizing again in specially constructed furnaces, shown

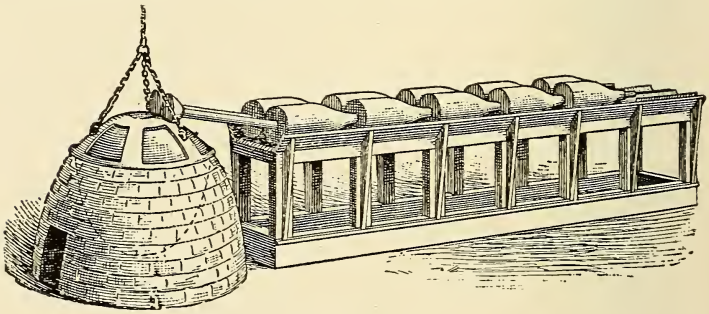


Fig. 30.—Apparatus for purifying iodine by sublimation.

in Fig. 30. In recent years probably more of the iodine supply has come from the deposits in Chile; although during the late war in the manufacture of potassium and other compounds from kelp much iodine was obtained as a by-product.

21. **Physical Characteristics.**—Iodine is a lustrous, nearly black solid. It crystallizes in thin plates, which even at room temperature are volatile, as may be seen if the crystals are placed in a white dish. Upon warming gently it vaporizes without melting. The process is called *sublimation* and is used for purifying iodine and

other substances which pass directly from the solid to the gaseous condition upon heating. It corresponds to the distillation of liquids. For medical purposes iodine is sublimed more than once as is indicated by the labels upon the bottles marked, *resublimed.* Iodine has an odor resembling dilute chlorine. It is very slightly soluble in water, barely sufficient to color the solution. However, in a solution of potassium iodide in water iodine is very soluble, giving a dark brown color. The same is true of alcohol and ether solutions, in both of which liquids it is very soluble. Carbon disulphide is also an excellent solvent and gives a beautiful violet solution; starch mucilage is turned deep blue, a reaction which serves as the test both for iodine and starch, as may be needed. The quantity of iodine should be small, just sufficient to give the solution a pale yellow color; otherwise, the starch will turn so dark it will appear black. To the eye weak solutions of iodine appear not unlike those of bromine. They may be distinguished by adding 1 or 2 c.c. of carbon disulphide to the solution of iodine or bromine and shaking well. As the carbon disulphide is a much better solvent than the water, the bromine or iodine will be collected in the small quantity of the heavy carbon disulphide at the bottom of the test tube. The bromine will give a golden brown and the iodine a purple color.

22. **Chemical Characteristics.**—These resemble those of chlorine, but are much feebler. A crystal of iodine laid upon a thin slice of phosphorus reacts vigorously so that the phosphorus catches fire and burns, while considerable of the iodine is vaporized. Iodine is readily displaced from soluble compounds by both chlorine and bromine, but much more easily by the former. Thus,

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

Even a single bubble of chlorine causes a brown discoloration of the liquid. A very interesting fact about iodine is its behavior at high temperatures. In a preceding section in this chapter the atomic weight of iodine was mentioned as about 127. Its molecular weight is found to be 254, which shows that like chlorine and bromine it is diatomic. When heated above 700° C. the vapor becomes lighter and lighter, much more so than agrees with Charles' law, until at 1,700° it is just half what it was at 700. This indicates that the molecules have been broken into two parts and that the gas is now monatomic. The same is true of bromine vapor, but to a considerably less extent. It must be noted further that as the temperature is lowered the lighter molecules recombine to form the diatomic molecules; at the same time a very considerable amount of heat is evolved, just as when steam is cooled it gives off the heat previously consumed in producing it. The following equation illustrates what is happening,

$$I_2 \rightleftarrows 2I.$$

The double arrow sign used is read, *gives reversibly.* Such changes are called *dissociation,* a term which means the process of decomposing a substance and reforming it under varying conditions. It is probable that at all temperatures, between 700 and 1700, the action is proceeding in both directions, that is, some of the diatomic molecules are being decomposed and others are being reformed by the union of two monatomics.

23. **Uses.**—Iodine is used mainly in medicinal preparations. The tincture, the best known, an alcoholic solution, is used as a counter-irritant in sprains, bruises and swellings; as a germicide in preventing the spread of erysipelas and other similar diseases; as an antiseptic in surgical operations and wounds in place of hydrogen

peroxide. It is more powerful, more penetrating and more lasting, than the peroxide, but at the same time much more severe, causes much more irritation, and in unskilled hands is much less safe. Iodoform, $CHI_3$, is a pale-yellow solid; has a peculiar odor, disagreeable to most individuals; is strongly germicidal, and often used by physicians as an antiseptic in contagious diseases. Iodothyrin, an extract obtained from the thyroid gland of sheep is sometimes used in cases of underdevelopment of the same gland in the human body.

### Exercises for Review

1. Name the halogens and state why so called.
2. Who discovered chlorine? What was the discoverer's idea regarding it? What was the old name? Who proved it was an element?
3. Give usual method of preparing and collecting chlorine.
4. Describe one commercial method of obtaining chlorine.
5. Give the physical characteristics of chlorine.
6. Give the chemical characteristics.
7. Name the important uses of chlorine.
8. How is hydrogen chloride prepared? Give its characteristics.
9. How is hydrochloric acid prepared? What is muriatic acid?
10. Give the characteristics of hydrochloric acid.
11. What can you say of the history of it? Name some uses.
12. What is aqua regia? Why so called?
13. Give the uses of hydrofluoric acid. How is it kept for use?
14. What can you say of the occurrence of bromine?
15. How is bromine prepared for commerce? Compare method with that of chlorine.
16. Describe bromine. What danger in handling it?
17. What is the chief use of bromine?
18. Where is iodine found? How prepared?
19. Give the principal characteristics of iodine—physical and chemical.
20. What is sublimation? How is it different from distillation?
21. Give uses of iodine and iodine compounds.

## CHAPTER X

## ACIDS AND BASES

**Outline—**

- Oxides, Basic and Acidic
- Acids
- Bases
- Nomenclature of Compounds
  - (*a*) Acids
  - (*b*) Bases
- Neutralization
- Salts
  - (*a*) Normal or Neutral
  - (*b*) Acid
  - (*c*) Basic
  - (*d*) Nomenclature
  - (*e*) Binary

1. **Oxides.**—An oxide is a compound consisting of only two elements one of which is oxygen. Since oxygen combines with all the elements except fluorine and the argon group, we should expect there would be a very large number. Already we have met with several. Mercuric oxide has been used in preparing oxygen; manganese dioxide as a catalyst in making oxygen and in the preparation of chlorine, bromine and iodine. Whenever we have burned a metal in oxygen or the air, as for example iron or magnesium, we obtained an oxide. Likewise, when phosphorus and sulphur were burned in oxygen or in the air their oxides were produced.

2. **Two Classes of Oxides.**—If oxides, such as will react with water, are put with water, some will be found to give a sour taste, and will turn litmus paper red, while others thus treated, have a soapy taste and turn reddened litmus paper blue. When Lavoisier gave the

name, *oxygen,* meaning acid former to the gas, he did not recognize the fact that a chemical change takes place between certain oxides and water, but considered the oxides themselves as acids. Such oxides as react with water to form acids are called *acidic* oxides, or *anhydrides,* and those that form hydroxides with the water are called *basic* oxides. Typical of the former class are those obtained when sulphur and phosphorus were burned in oxygen. With water they react thus,

$$SO_2 + H_2O \rightarrow H_2SO_3,$$
$$P_2O_5 + H_2O \rightarrow 2HPO_3.$$

The most familiar basic oxide is lime. When treated with water vigorous chemical action results accompanied by great heat. The equation is

$$CaO + H_2O \rightarrow Ca(HO)_2$$

Similar reactions are those of sodium and potassium oxides with water,

$$Na_2O + H_2O \rightarrow 2NaHO,$$
$$K_2O + H_2O \rightarrow 2KHO.$$

A careful study of the various oxides shows that, generally speaking, those of the metals react with water more or less rapidly to produce *bases,* while those of the nonmetalic elements are anhydrides, or acid-forming oxides.

3. **Acids.**—It has been said elsewhere that all acids contain hydrogen. Most of them also contain oxygen. If all were formed by the union of an oxide with water, all would necessarily contain oxygen. A few, such as the acids of the halogens, hydrofluoric and others, are solutions of certain compounds and are not formed by the interaction of some oxide with water. In all of them, however, the hydrogen forms the positive part of the compound, while the other element together with

the oxygen when present, constitutes the negative part. It is the hydrogen in a peculiar condition which will be discussed later that causes all acids to turn litmus red.

4. **Bases.**—Theoretically, at least, all bases may be formed by the interaction of a metallic oxide and water; naturally therefore, all must contain a metal, hydrogen and oxygen, since the action is an additive one. They are all called *hydroxides,* a term which indicates that they contain hydrogen and oxygen. There is no exception to this. One base is known, however, which contains no metal, ammonium hydroxide, $NH_4HO$, but the chemical group, $NH_4$—shows many of the characteristics of a metal. The soluble bases are called *alkalies;* they are potassium hydroxide, sodium hydroxide, ammonium hydroxide, and those of barium, strontium and calcium. The blue litmus test which they give is due to the hydroxyl group, HO, which they all contain, and which is the only thing common to all.

5. **Nomenclature.**—Little need be said about how bases are named. They are all called hydroxides with the name of the metal prefixed, thus: $Cu(HO)_2$ is called copper hydroxide and $Al(HO)_3$ is aluminum hydroxide. In a preceding chapter the gas, HCl, has been spoken of as hydrogen chloride. This is for the reason that when perfectly free from water it shows no acid properties. Likewise, we should expect a compound with the formula $H_2SO_4$ to be called hydrogen sulphate; $H_2CO_3$, hydrogen carbonate; $HNO_3$, hydrogen nitrate. They are all acids as the formulas indicate and this plan would be in accordance with what has been said in Chapter I. Attempts have been made to adopt such a nomenclature, but as several of the familiar acids were discovered and in common use before there was any system in the naming of com-

pounds, such efforts have met with failure. Accordingly, in the oxygen acids the electronegative element suggests the name. Thus, in the three given above, sulphur, carbon and nitrogen have given the respective names. This is true, generally. However, there are many cases in which there are two or more acids formed from the same three elements. Thus sulphur has

| | |
|---|---|
| $H_2SO_4$ | Sulphuric, |
| $H_2SO_3$ | Sulphurous, |
| $H_2SO_2$ | Hyposulphurous, |

and chlorine forms

| | |
|---|---|
| $HClO_4$ | Perchloric, |
| $HClO_3$ | Chloric, |
| $HClO_2$ | Chlorous, |
| $HClO$ | Hypochlorous. |

In such case the quantity of the oxygen determines the ending of the name. It is usually true that the most common acid in any group has a name ending in *ic;* then, the one with a smaller amount of oxygen next to this is given the same name with the ending changed to *ous.* If there be others, the prefixes *hypo,* meaning *under,* and *per,* meaning *beyond* or *above,* are used. This is seen in the four chlorine acids given above. In the case of the acids containing no oxygen the prefix *hydro* is used in all cases, thus,

| | |
|---|---|
| $H_2F_2$ | Hydrofluoric, |
| $HCl$ | Hydrochloric, |
| $HBr$ | Hydrobromic, |
| $HI$ | Hydriodic |
| $H_2S$ | Hydrosulphuric. |

6. **Neutralization.**—If a base and an acid are brought together in suitable proportions, chemical action takes place, in which both are destroyed and new

compounds are formed. The process is called *neutralization,* for the reason that when the two are exactly proportioned the compound resulting affects *neither* red nor blue litmus paper. The following equations illustrate a few cases,

$$Ca(HO)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O,$$
$$KHO + HCl \rightarrow KCl + H_2O,$$
$$Ba(HO)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O,$$
$$NaHO + HNO_3 \rightarrow NaNO_3 + H_2O,$$
$$2NaHO + H_2CO_3 \rightarrow Na_2CO_3 + 2H_2O.$$

It will be noticed in all these cases that one of the products is water. The other is a compound which is not a base since it does not contain *hydroxyl;* it is not an acid since it has no *positive* hydrogen. It is a new compound. All such, produced by the union of a base and an acid, or by a similar process, are called *salts.* This name was given for the reason that a very large number of them resemble common salt and may be formed the same way.

7. **Classes of Salts.**—All those shown in the equations just above are called *neutral* or *normal* salts, because the hydrogen has all been removed from the acid and the hydroxyl from the base, so that generally speaking they should affect neither red nor blue litmus. However, such proportions of the acid or base might be used as to leave some hydrogen from the acid or some hydroxyl from the base not thus neutralized. For example,

$$H_2SO_4 + NaHO \rightarrow NaHSO_4 + H_2O,$$
$$H_3PO_4 + NaHO \rightarrow NaH_2PO_4 + H_2O,$$
$$H_3PO_4 + 2NaHO \rightarrow Na_2HPO_4 + 2H_2O,$$
$$H_3PO_4 + 3NaHO \rightarrow Na_3PO_4 + 3H_2O.$$

In three of the above equations some of the hydrogen remains in the salt obtained and should give the test. In fact, frequently in such salts the sour taste of the acid is

still very noticeable and blue litmus is quickly reddened. All such are called *acid salts*: they are very common. Obviously such an acid as hydrochloric could not form an acid salt. It must be observed further, that not all salts containing hydrogen are acid salts. Thus,

$$NH_4HO + HNO_3 \rightarrow NH_4NO_3 + H_2O,$$
$$NaHO + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O.$$

Both the salts formed in these equations contain hydrogen, yet both are neutral salts. In both cases all the *positive* hydrogen has been removed from the acid. In the first one, the hydrogen remaining in the salt was obtained from the base, and belongs to the group, $NH_4$. In the second, only the hydrogen atom written by itself is positive: the other three are combined in the group $C_2H_3O_2$ which is a radical and the hydrogen is not free to act alone. On the other hand, there might be more hydroxyl groups present in the base used than the hydrogen in the acid could remove in the formation of water. Thus,

$$2Cu(HO)_2 + H_2CO_3 \rightarrow 2H_2O + Cu_2(HO)_2CO_3.$$

Usually this is written $CuCO_3.Cu(HO)_2$. Such salts are not as common as the acid salts, but they do appear and are formed in various ways. They are called *basic* salts. The above is called basic copper carbonate.

8. **Nomenclature of Salts.**—The common salts offer no difficulties to the student in their nomenclature. Thus,

| | |
|---|---|
| KBr | Potassium bromide |
| $ZnCl_2$ | Zinc chloride |
| $K_2S$ | Potassium sulphide |
| $CuSO_4$ | Copper sulphate |
| $NaNO_3$ | Sodium nitrate |
| $CaCO_3$ | Calcium carbonate, |

$KClO_3$ Potassium chlorate,
$Na_3PO_4$ Sodium phosphate,
$KIO_3$ Potassium iodate,
$KBrO_3$ Potassium bromate.

Compounds with two elements have names ending in *ide;* while the others end in *ate* unless formed from an acid whose ending is *ous* when the salt has a name ending in *ite*. The difficulty is with the compounds formed from the same three elements used in different proportions. Thus,

$Na_2SO_4$ Sodium sulphate, formed from $H_2SO_4$ sulphuric acid,

$Na_2SO_3$ Sodium sulphite, formed from $H_2SO_3$ sulphurous acid,

$Na_2SO_2$ Sodium hyposulphite, formed from $H_2SO_2$, hyposulphurous acid,

and

$KClO_4$ Potassium perchlorate from $HCl_4$ perchloric acid,
$KClO_3$ Potassium chlorate from $HClO_3$ chloric acid,
$KClO_2$ Potassium chlorite, from $HClO_2$ chlorous acid,
$KClO$ Potassium hypochlorite, from $HClO$ hypochlorous acid.

Only memorizing the formulas of the acids in the series, and the fact that oxygen acids ending in *ic* give salts ending in *ate;* and ending in *ous,* salts ending in *ite* can suffice. However, most of these are not of sufficient importance in warranting the beginner in making the attempt. Again, the acid salts offer some trouble, thus,

$K_2SO_4$ is potassium sulphate,

$KHSO_4$ is acid potassium sulphate or potassium hydrogen sulphate. As there can be only one acid potassium sulphate no confusion results from the use of either term.

But *tribasic* acids, like phosphoric, $H_3PO_4$, yield two acid salts, thus,

$K_3PO_4$ Potassium phosphate,
$K_2HPO_4$ Dipotassium phosphate,
$KH_2PO_4$ Monopotassium phosphate.

As the last two are both acid salts they could not be read *acid potassium phosphate*, for either might be meant. It is customary, therefore, to follow the plan suggested, in which the amount of the base used is indicated by the prefix *di* or *mono*. The fact that one hydrogen remains from the acid in the salt is implied by the prefix *di*, for the reason that the acid originally contained three hydrogen atoms and only two have been replaced. Likewise, *mono* implies that two atoms of hydrogen remain in the salt.

9. **Binary Salts.**—Compounds of two elements are called binaries. Such are all salts made from the binary or no-oxygen acids. Their nomenclature offers no difficulty except in cases of two or more formed from the same two elements. When such is the case, the endings, *ous* and *ic* are used just as has been said in the acid endings. The one ending in *ous* always indicates the one *full of* or having the greater *relative* amount of the positive part of the compound. Thus,

$Hg_2O$ Mercurous oxide,
$HgO$ Mercuric oxide,
$FeCl_2$ Ferrous chloride,
$FeCl_3$ Ferric Chloride,
$HgCl_2$ Mercuric chloride,
$Hg_2Cl_2$ Mercurous chloride,
$SnO_2$ Stannic oxide,
$SnO$ Stannous oxide.

Oftentimes prefixes are used which may lessen the dif-

ficulty. Thus, manganese *di*oxide indicates the amount of the oxygen; again old forms, now obsolete, are sometimes used which are often obscure. Thus, $Fe_2O_3$ is sometimes called iron *sesquioxide*, instead of ferric oxide. The prefix means a ratio of *two to three* and was applied to such compounds as the one just given. *Proto* and *sub*, meaning the *first* and *under* are also used applied to the lowest of the compounds in a series.

### Exercises for Review

1. What is an oxide? Name two classes, define each and give examples.

2. What can you give for the composition of acids? What two tests do they give?

3. Give the composition of bases? What tests do they give?

4. What is an alkali? Name five.

5. How are bases named? Acids?

6. Give names of $HClO_3$, $HIO_3$, HBr, $HBrO_3$, $H_2SO_4$, $H_3PO_4$, $Ba(HO)_2$, $Ca(HO)_2$ NaHO.

7. What is meant by neutralization? Write an equation illustrating.

8. Complete the following equations:

$$H_2SO_4 + Cu(HO)_2 \rightarrow ,$$
$$HCl + Ba(HO)_2 \rightarrow ,$$
$$CaO + H_2SO_4 \rightarrow ,$$
$$Zn(HO)_2 + H_2SO_4 \rightarrow ,$$
$$ZnO + H_2SO_4 \rightarrow ,$$
$$Zn + H_2SO_4 \rightarrow .$$

9. How many salts were obtained in the above equations? Were any formed without the use of a base? Why was this?

10. What is a salt? Name three kinds. Define each and give examples.

11. Which of the following are acid salts: $KNO_3$, $KHSO_4$, $CuSO_4$, $AgNO_3$, $K_2HPO_4$, $KH_2PO_4$, $K_3PO_4$, $CaH_2(CO_3)_2$?

12. Give names of all formulas in question 11.

13. What is a binary compound? Illustrate.

14. Give names of FeO, $Fe_2O_3$, $FeCl_3$, $FeCl_2$, CuS, $Cu_2S$, $H_2O$, $H_2O_2$, $Hg_2O$, HgO.

# CHAPTER XI

## NITROGEN AND COMPOUNDS

**Outline—**

- Nitrogen
  - (*a*) Occurrence
  - (*b*) Preparation from the Air
  - (*c*) Preparation from Chemicals
  - (*d*) Characteristics
- Ammonia
  - (*a*) Occurrence
  - (*b*) Commercial Supply
  - (*c*) Uses
- Oxides of Nitrogen
- Nitric Acid
  - (*a*) Preparation
  - (*b*) Characteristics
  - (*c*) Uses
- Explosives
  - (*a*) Gunpowder
  - (*b*) Nitroglycerine
  - (*c*) Dynamite
  - (*d*) Nitrocellulose
  - (*e*) Smokeless Powders
  - (*f*) Picrates
  - (*g*) T.N.T.
- Other Products
  - (*a*) Collodion
  - (*b*) Celluloid
  - (*c*) Fiber Silk

1. **Occurrence of Nitrogen.**—In another chapter it has been seen that nitrogen constitutes about four-fifths of the air. It is found in many compounds in nature, especially the nitrates of sodium and potassium. The former occurs in large quantities in Chile, whence it is

exported to all parts of the world. Nitrogen is an important constituent of such food products as lean meat, eggs, beans and peas, and is found to some extent in grains, wood, coals and like substances. Some varieties of coal contain in the neighborhood of 2 per cent.

2. **Preparation.**—By removing the other constituents of the air, nitrogen may be obtained comparatively pure except for the admixture of the argon. This is generally done by the use of phosphorus or by passing a stream of air over heated copper turnings. The proportion of nitrogen in the air may be shown somewhat approxi-

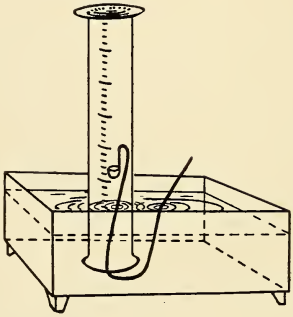


Fig. 31.—Method of determining approximately the proportion of nitrogen in the air.

mately by apparatus shown in Fig. 31. A graduated cylinder is inverted over a deflagrating spoon with handle bent as shown. Into the spoon is put a piece of yellow phosphorus the size of a small bean; then the whole is placed over a trough of water and the cylinder clamped so that the water level inside and out is at the zero mark. The phosphorus will slowly combine with the oxygen and at the end of two or three days the water level will have become stationary except for atmospheric changes of pressure and temperature. The

volume of the residual nitrogen and argon may then be read off. From compounds nitrogen is generally prepared by gently heating a solution of ammonium chloride and sodium nitrite. The following equations illustrate the changes taking place,

$$NH_4Cl + NaNO_2 \rightarrow NaCl + NH_4NO_2,$$
$$NH_4NO_2 \rightarrow N_2 + 2H_2O.$$

3. **Characteristics of Nitrogen.**—Nitrogen is a colorless gas, slightly lighter than air, may be liquefied at –194° C. and solidified at –214° C. It is much less soluble in water than oxygen. Chemically, it is a very inactive element; it will not burn or combine with many of the elements directly. Passed over strongly heated magnesium or calcium it will form a nitride with them. It was by passing nitrogen over heated magnesium that argon was discovered, since it will not combine with magnesium. By means of a powerful electric discharge through a mixture of oxygen and nitrogen, chemical union takes place between these two elements with the formation of one or more oxides of nitrogen. Likewise a mixture of hydrogen and nitrogen, three parts to one, by means of the electric spark is slowly changed into ammonia. The uses of nitrogen have been discussed in the chapter on the atmosphere.

4. **Occurrence of Ammonia.**—Because of the fact that certain waste products of the animal economy, as well as other nitrogenous bodies in their decomposition, produce ammonia in appreciable quantities, it has long been familiar to scientists. For many years it was sold in solution under the name "spirits of hartshorn" because of the fact that it was formerly obtained by the distillation of the horns of deer and cattle.

5. **Commercial Supply.**—Some varieties of ordinary soft coal contain nitrogen in appreciable quantities, in

the form of compounds. When such coals are heated the nitrogenous bodies are decomposed and the nitrogen comes off as ammonia, $NH_3$, mixed with a great variety of other gases. On account of its high solubility it may be largely separated from the others by passing through towers or cylinders containing coke or something similar, kept moist by dripping water. This very impure solution, called *gas liquor* is drawn off, lime is added and the mixture is boiled. The ammonia distils out and is passed into either hydrochloric or sulphuric acid, when the chloride or sulphate of ammonia is formed,

$$NH_3 + HCl \rightarrow NH_4Cl,$$
$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4.$$

By treating a solution of either of these salts with lime and passing the gas into distilled water, pure ammonium hydroxide or aqua ammonia is obtained,

$$(NH_4)_2SO_4 + CaO \rightarrow CaSO_4 + 2NH_3 + H_2O,$$
$$NH_3 + H_2O \rightarrow NH_4HO.$$

6. **Characteristics of Ammonia.**—Ammonia is a colorless gas, with very pungent odor. It is exceedingly soluble in water so that about 1,200 liters will dissolve in 1 liter of water at 0° C. Putting it into other words, one quart of ice water will absorb nearly six barrels of ammonia gas. It may be liquefied at –38.5 C. and solidified at –77° C. The strong ammonia water of commerce contains about 35 per cent of the gas with a specific gravity of 0.88. At ordinary temperatures, except under pressure, water will hold only about 28 per cent of ammonia, and at 100° the ammonia is entirely expelled.

7. **Uses of Ammonia.**—Its principal use is in the liquid form for refrigeration purposes. From a container the liquid is allowed to pass through a needle valve into pipes surrounded by a solution of salt, of such strength

that its freezing point is much lower than that of pure water. A pump is constantly withdrawing the gasified ammonia, thus maintaining a partial vacuum, so that a rapid evaporation of the ammonia is secured. The rapidity of the evaporation causes a lowering of the temperature of the pipes and the surrounding brine, which is kept circulating by a special brine pump. For cold storage purposes this brine is forced through pipes to any place desired: in this way meats, fruits, but-

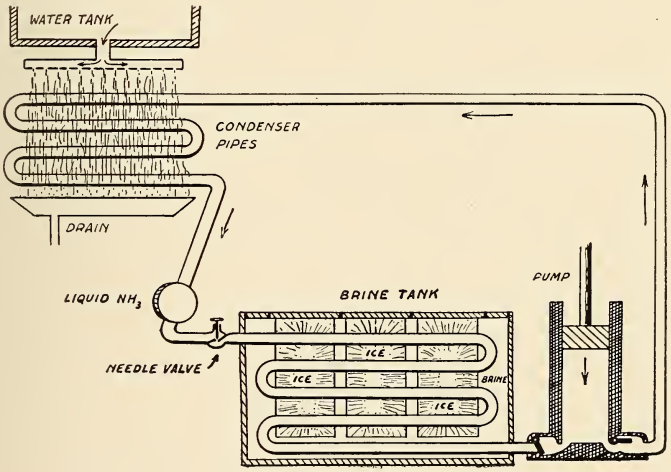



Fig. 32.—Manufacture of ice.

ter, eggs, and all other perishable food products may be kept near the freezing point for long periods. For protection against moths, furs and woolen clothing are often stored thus in the summer. Temperatures low enough to freeze meats may easily be secured; fishing vessels, gone on long trips, often return after months with their cargo of fish frozen solid. Markets, floral shops, and various other places employ these methods of preserving

their goods; everyone has seen the brine pipes, heavily coated with frost, which furnish the cold for such purposes. For the manufacture of ice, galvanized iron boxes filled with pure water are lowered into the brine tank. In from sixty to seventy-two hours the water has become solid, whereupon the container with the ice is lifted from the brine; a stream of warm water is run over it for a moment to loosen the ice, when it slips out and slides down into the storage room. Fig. 32 shows the main steps in the process. When the ammonia is withdrawn from the pipes it is again compressed and in summer time is cooled by streams of running water, whereby it again becomes a liquid. It is said that to make 3 pounds of ice requires about 1 pound of ammonia, but as the liquid is used over and over again the process is very cheap. In the household, ammonia is often used in a dilute solution for softening water and for similar purposes. In commerce it finds extensive use in the manufacture of cooking soda and of sodium carbonate. The process will be described elsewhere in the text.

8. **The Oxides.**—There are five oxides of nitrogen known. They are:

Nitrous oxide, Nitrogen monoxide, $N_2O$,
Nitric oxide, Nitrogen dioxide, NO, sometimes written $N_2O_2$,
Nitrous anhydride, Nitrogen trioxide, $N_2O_3$,
Nitrogen peroxide, Nitrogen tetroxide, $NO_2$, also written, $N_2O_4$,
Nitric anhydride, Nitrogen pentoxide, $N_2O_5$.

About the only facts of interest regarding the third and fifth in the series are that they are the anhydrides of acids, thus,

$$N_2O_3 + H_2O \rightarrow 2HNO_2, \text{ Nitrous acid,}$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3, \text{ Nitric acid.}$$

Nitric oxide is mentioned for the reason that almost invariably when nitric acid is added to a metal, it is produced. However, it is never seen unless precautions are taken to collect it over water, because of the fact that as soon as exposed to the air it combines spontaneously with oxygen and forms the tetroxide. Thus,

$$3Cu + 8HNO_3 \rightarrow 2NO + 4H_2O + 3Cu(NO_3)_2;$$
$$2NO + O_2 \rightarrow 2NO_2.$$

The peroxide is a heavy, reddish-brown gas resembling bromine vapor, with very irritating odor. It is very soluble in water with which it reacts, thus,

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2.$$

9. **Nitrous Oxide.**—Nitrous oxide may be prepared by cautiously heating ammonium nitrate, thus,

$$NH_4NO_3 \rightarrow N_2O + 2H_2O.$$

As it is somewhat soluble in cold water it must be collected over warm water. It is a colorless gas, with a very faint pleasant odor. In it various substances will burn when ignited almost as well as in oxygen and a spark on a pine splinter will burst into flame. It becomes a liquid at about –90° C. and a solid at –102° C. If inhaled it produces insensibility and mixed with oxygen it is frequently used as an anesthetic for minor surgical operations such as the extraction of teeth. It is sometimes called *laughing gas*, because of its intoxicating effects upon some individuals.

10. **Nitric Acid.**—It is said that occasionally, after unusually violent electrical storms accompanied by little rain, traces of nitric acid have been found in the water which has fallen. As nitric acid is an oxyacid it should be able to be formed in this manner.

11. **Commercial Preparation.**—In the laboratory and commercially up to very recent times nitric acid has

always been prepared by treating sodium nitrate with sulphuric acid, thus,

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3.$$

The laboratory form of apparatus is shown in the illustration. No corks, either rubber or otherwise, may be used as they are rapidly attacked by the fumes. From the fact that during the war, trade with Chile was largely interrupted so that adequate supplies of sodium nitrate could not be obtained, other methods had to be adopted. Consequently, preparation from the air during the last years of the war was carried on extensively. At points where electricity of high voltage could be ob-

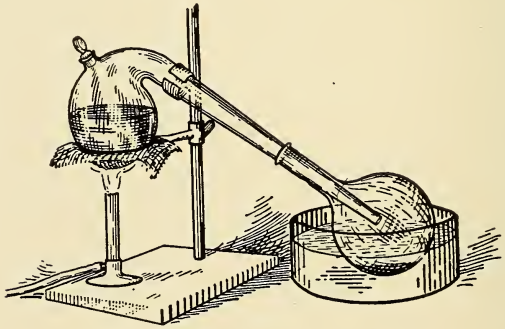


Fig. 33.—Preparation of nitric acid.

tained cheaply from water power, by electric discharge through a slowly moving current of air, certain oxides of nitrogen are obtained. These are passed into water with the formation of nitrous and nitric acid,

$$H_2O + N_2O_3 \rightarrow 2HNO_2,$$
$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3,$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3.$$

As nitrous acid readily takes up more oxygen and becomes nitric, the ultimate product is nitric. It is prob-

able that this method in some form will eventually displace the older one of obtaining nitric acid from saltpeter.

12. **Characteristics of Nitric Acid.**—When pure, nitric acid is a colorless liquid, but exposed to bright sunlight, or heated, decomposition takes place with the formation of sufficient peroxide to color the liquid more or less brown. It boils at 86° C. and solidifies at –47° C. The concentrated acid of commerce contains 68 per cent nitric acid, with a specific gravity of 1.42. Upon the hands or clothing it produces a yellowish-brown stain, which cannot be removed by ammonia as can those of hydrochloric acid. It is a strong oxidizing agent, for reasons shown by the equation,

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O.$$

From the fact that it thus readily yields free oxygen it reacts differently with metals from that of other acids thus far mentioned. Instead of giving up hydrogen as do hydrochloric and sulphuric, when put with a metal, as iron or zinc, it converts the metal into an oxide. Then, this oxide often dissolves in other portions of the acid present and forms a nitrate. For example, copper reacts with nitric acid forming copper nitrate, $Cu(NO_3)_2$ and nitric oxide and water but no hydrogen. The changes which may be presumed to take place may be represented thus,

$$3Cu + 2HNO_3 \rightarrow 3CuO + H_2O + 2NO,$$
$$3CuO + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 3H_2O.$$

Adding the two equations together we have the result as obtained by the actual experiment,

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

13. **Uses.**—One of the most important uses of nitric acid is in the manufacture of explosives. Gunpowder,

while not made from nitric acid, contains potassium or sodium nitrate, both of which are salts of nitric acid. The other constituents are sulphur and charcoal, but the nitrate forms 75 per cent of the whole. Being a mixture, an appreciable length of time is required for the combustion to proceed throughout the entire mass; hence, gunpowder is a low power explosive. Among those of high power, glyceryl nitrate, commonly called nitroglycerine, is one of the longest known. It is prepared by treating glycerine with fuming nitric acid. The reaction,

$$C_3H_5(HO)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O,$$

shows that for every molecular weight of nitroglycerine produced there are three of water formed. In a short time this would so dilute the nitric acid that chemical action would cease, or become exceedingly slow. It becomes necessary, therefore, to remove it. This is done by introducing continuously with the nitric acid fuming sulphuric, which as we have seen is a great absorbent of water. In this way the process becomes continuous. Nitroglycerine is a heavy, oily liquid, and for this reason not convenient to handle or transport. Much of it is therefore made into dynamite or giant powder and other explosives. By mixing with it sawdust or *kieselguhr,* a silicious earth of tubular structure, both of which have high absorbtive powers for nitroglycerine, dynamite is prepared. It is commonly sold under the name of giant powder with percentages of nitroglycerine ranging from 25 to 75. It is used in the form of sticks or in coarse granules. Such explosives as these are fired by a *detonator*, such as mercuric fulminate, $Hg(CNO)_2$, commonly called *fulminating mercury.* This compound is decomposed by a sharp blow, giving a spark and heat sufficient

to begin the decomposition of the main explosive. All explosives contain combustible material and within themselves oxygen sufficient or nearly so to burn completely. In two nitroglycerine molecules, $2C_3H_5(NO_3)_3$, there are 6 atoms of carbon and 10 of hydrogen. The hydrogen requires 5 atomic weights of oxygen for its combustion and the carbon 12. By looking at the formula it will be seen that the oxygen is a little more than sufficient, as the nitrogen is set free and passes off in this condition. It is apparent, therefore, that the liquid or solid, excepting the inert material used, is entirely converted into gases of very great volume, which through the heat generated are enormously expanded; coming almost instantaneously the pressures are tremendous and the results terrific.

14. **Nitrocellulose.**—This is commonly called guncotton. Cellulose, of which filter paper or cotton is largely composed, has the formula, $(C_6H_{10}O_5)_n$. Into this molecule we may introduce nitrate groups as in the case of the glycerine and by the same method. Water is a by-product and must be removed as before. In this case any number of nitrate groups may be substituted, from three to six, the hexanitrate being much more explosive than the compounds with fewer nitrate groups. The following equation shows the reaction,

$$2C_6H_{10}O_5 + 6HNO_3 \rightarrow C_{12}H_{14}O_4(NO_3)_6 + 6H_2O.$$

The products of the explosion are the same as before. Guncotton is safe to handle if kept damp and in this condition it is uniformly transported on shipboard or elsewhere. Even when damp it may be exploded by the use of a detonator or electric spark with a small amount of dry to start the process. It is used in mining harbors or other places against attack as well as for other simi-

lar purposes. The ternitrate, being much less explosive, when dissolved in a mixture of alcohol and ether, is sold under the name *collodion.* It is a viscous, quick-drying liquid, used in photography, and as *new skin,* so-called, in medicine. For the latter purpose a small per cent of Venice turpentine and castor oil is added to render it more flexible and less liable to crack when dried upon the skin. If a solution of camphor in alcohol is used as a solvent for the guncotton, *celluloid* is obtained, the uses of which are familiar. *Fiber silk* is another product closely related. The guncotton, by one method, is dissolved as in making collodion: when it has reached

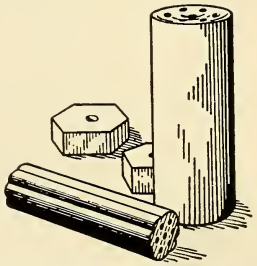


Fig. 34.—Some forms of smokeless powder.

a thick, viscous stage it is forced through tiny openings like those in the spinneret of the spider or silk worm. These threads dry instantly upon coming into the air, are wound on bobbins and made into cloth as if real silk. The explosive nitrate groups must be removed and this is done by treatment with an alkali or with calcium sulphide. The luster is not greatly different from that of real silk, but the fibers are more brittle and the wearing qualities as a result inferior.

15. **Smokeless Powders.**—Two varieties are sold under the names, *cordite* and *ballistite.* The former is a mixture

of nitroglycerine and guncotton with a little vaseline added. Ballistite is a mixture of the same two explosives to which is added a small amount of diphenylamine, which reduces the explosive character. Other varieties are simply the hexanitrate cellulose dissolved and molded into various shapes, some of which are shown in Fig. 34.

16. **Picric Acid and T. N. T.**—Picric acid with the formula, $C_6H_2(NO_2)_3OH$, is obtained from phenol, commonly known as carbolic acid, $C_6H_5OH$, in which have been substituted three *nitro* groups for three of the hydrogen atoms. This will be seen by examining the two formulas. It is a very explosive substance and from it a very considerable number of high explosives have been prepared. An intimate mixture of red lead, $Pb_3O_4$, with about an equal volume of picric acid makes a powerful explosive which may be fired by heat alone. During the war a great deal was heard about the explosive, T.N.T. and its terrific power. Toluol is a compound closely related to phenol, with the formula, $C_6H_5CH_3$. The group, $CH_3$, has taken the place of hydroxyl, HO, in the phenol. T.N.T. is trinitrotoluol, with the formula, $C_6H_2(NO_2)_3$-$CH_3$, which will be observed is toluol with three hydrogen atoms replaced by nitro groups. When exploded the products are not essentially different from those already described elsewhere.

### Exercises for Review

1. State where nitrogen occurs in nature. What food products contain it?
2. How is nitrogen obtained from the air? How from chemicals?
3. Describe nitrogen. How was argon discovered?
4. How do you account for the presence of ammonia in the air?
5. What is spirits of hartshorn?
6. State how ammonia is prepared for commerce. Write the equations.

7. Describe ammonia.

8. Give important uses of ammonia.

9. Name the oxides of nitrogen and give formulas.

10. How is nitrous oxide prepared? Chief use?

11. How is nitric acid prepared? Equation.

12. Explain how nitric acid is made synthetically. What led to this?

13. Give chief properties of nitric acid. Why is it an oxidizing agent?

14. Give important uses of nitric acid.

15. How is nitroglycerine made? Dynamite? When exploded, what forms?

16. What is nitrocellulose? Collodion? Celluloid? Fiber silk?

17. Name two smokeless powders. State how made.

18. What is T.N.T.?

# CHAPTER XII

## CARBON

Outline—

- Occurrence in Nature
- Allotropic Forms of Carbon
- Characteristics of Carbon
- Diamonds
  - (*a*) Origin
  - (*b*) Uses
- Graphite, Compared with the Diamond
  - Uses
- Coals, How Produced in Nature
  - Varieties
- Petroleum
  - (*a*) Origin
  - (*b*) Kinds
  - (*c*) Products obtained by Distillation
- Natural Gas
- Charcoal
  - (*a*) Kinds
  - (*b*) Uses
- Lampblack
- Coke
- Gas Carbon
- Carbon Monoxide
  - (*a*) Formation
  - (*b*) Characteristics
- Carbon Dioxide
  - (*a*) Preparation
  - (*b*) Characteristics
  - (*c*) Uses
- Other Carbon Compounds

1. **Occurrence of Carbon.**—The relative amount of carbon in nature is not large. It will be remembered that it is not among the eight most abundant elements

which constitute almost the entire amount of the matter composing the earth. However, in the form of compounds it is familiar in a very great variety. In fact, so numerous are they that they constitute an entirely separate branch of chemistry, called *organic*, for the reason that years ago they were supposed to be produced by *organized* or life forces alone. The muscles of the body consist largely of proteins, composed mainly of carbon, hydrogen, oxygen and nitrogen. The stems of plants and trunks of trees are largely cellulose, containing carbon, hydrogen and oxygen. The mineral world furnishes the corals, limestone, marble, calcite, dog tooth spar, and many other carbon compounds. It is some form of carbon that constitutes the fuel of the world; carbon compounds in the form of starches, sugars and fats furnish heat and energy for the human body, while protein foods, similar compounds of carbon containing nitrogen, are necessary to rebuild the wasted muscles. Carbon thus becomes a very interesting and a very important element.

2. **Forms of Carbon.**—The only pure form of carbon is the diamond. Graphite, however, although in appearance it is entirely different, is nearly pure; closely related are anthracite coal and the artificial forms, coke, charcoal, gas carbon and lampblack. Other varieties of coal contain less free carbon and more bituminous compounds of carbon, hydrogen and nitrogen. Graphite may be considered a crystallized, allotropic form of the diamond, and lampblack an amorphous or uncrystallized allotrope.

3. **Some General Characteristics.**—The physical properties of carbon are so entirely different in the three allotropic forms that they must be considered separately. The crystallized varieties will burn only at very high temperatures and in an atmosphere of oxygen; the

amorphous forms, especially the more impure, burn readily in the air without the addition of great heat. At high temperatures carbon combines with various elements to form carbides. It is a strong reducing agent also at red heat, that is it has the power of removing oxygen from its combination with metals. This equation will illustrate,

$$ZnO + C \rightarrow Zn + CO.$$

4. **Proofs for Composition of Diamond.**—If heated in the absence of air to a dull-red temperature the diamond expands considerably, becomes lighter, and turns dark in color. If put into a tube, as shown in Fig. 35, with the air replaced by oxygen, and heated to bright redness, the diamond disappears and leaves only an at-

Fig. 35.—Burning of a diamond.

mosphere of carbon dioxide. A piece of graphite treated in the same way gives like results.

5. **Origin of Diamonds.**—Some believe that diamonds are of meteoric origin and not native to the earth, but of this there is little evidence. Undoubtedly they were formed under great pressure and a temperature sufficiently high to render the carbon more or less plastic, so that crystallization took place upon cooling. The great Kimberly mines of South Africa have been thought to be the crater of an extinct volcano, and some mines discovered in other places seem to be the same. The artificial diamonds made by Moissan some years ago point to the same theory as probably true. He mixed fine iron filings and charcoal made from sugar together,

put them into an electric furnace made from a block of lime, shown in Fig. 36, and by the electric arc melted the iron. It is well-known that molten iron will dissolve small amounts of carbon. So at this stage, Moissan plunged the mass into cold water, whereupon the iron solidified upon the outside, and by its contraction produced great pressure upon the interior. Thus the dissolved carbon crystallized under sufficient pressure to give it the density of the diamond, which is considerably above that of graphite. When cool the mass was broken up and the iron dissolved in nitric acid, leaving the diamonds unaffected. They possessed the hardness and

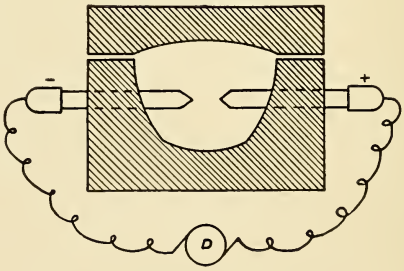



Fig. 36.—Moissan's electric furnace.

other characteristics of native diamonds, but were dark in color due to the presence of some uncrystallized particles of carbon. The experiment was of scientific interest, because of the fact indicated that if a source of heat sufficient to melt carbon is ever found artificial diamonds will become a possibility.

6. **Uses of Diamonds.**—Until it was discovered that diamonds could be cut and polished by their own dust, they never came into use as ornaments. Imperfect and discolored diamonds are used in various ways, because of their hardness; for example, in the bearings of fine

watches, delicate balances, for cutting glass, polishing other stones, on tips of drills, and other similar ways.

7. **Graphite.**—Next to the diamond graphite is the most nearly pure form of carbon. It occurs in nature, but not in sufficient quantities to meet the demands of commerce. Compared with the diamond it has a density of only 2.3, diamond being 3.5; it is a good conductor of electricity, the diamond poor; graphite occurs in six-sided plates, the diamond in regular octahedrons; graphite is a soft, greasy-feeling, black solid, the diamond the hardest mineral known, being 10 in the scale, and colorless. Since graphite is unaffected by the air it is used to give a finished coating to shot and the grains of both black and giant powder. It is an ingredient of most stove polishes, for the same reason. It is used in crucibles for melting very refractory substances and to give conductivity to wax plates in making electrotypes. Mixed with oil it is frequently used as a lubricant for bearings of heavy machinery. The most familiar of its many uses is in the so-called "lead pencil." This consists of a mixture of graphite and clay, proportioned in such a way as to give varying degrees of hardness from very soft to very hard. The clay and graphite mixed are moistened with water, made into a soft pliable mass and by pressure forced through small openings in metal plates. When dried these "leads" are ready for insertion in the wooden coverings familiar to all.

8. **Coals.**—Natural coals are believed to be the metamorphosed remains of the forests of another day. Growing at a time possibly when there was more carbon dioxide in the air than now, in a climate warm and moist, the forests undoubtedly surpassed in luxuriance and density anything known upon the earth at the present day. Swept down by some great catastrophe of nature

these forests were buried sufficiently deep to protect them from decay through access of the air and at the same time to subject them to heat and pressure. Under varying conditions of these two factors, a great variety of coals was formed, ranging from lignite, brown in color, soft, and often showing the original woody structure, to anthracite, hard, clean and lustrous. Intermediate between these are bituminous coals of great variety, rich in oily products, which burn with a yellow, smoky flame, and semianthracite with most of the bitumen expelled, which burns with but little smoke and but slightly yellow flame. Cannel coal is very rich in oily matter, not suitable for furnaces, but excellent for grate fires on account of the freedom with which it burns and the abundant yellow flames it gives. Peat is a modern variety of coal consisting largely of roots only partly changed, with the admixture of considerable earthy matter.

9. **Petroleum.**—From 30 to 40 per cent of some coals is an oily product. This may be easily expelled by heat. Undoubtedly anthracite and semianthracite coals were produced by the greater heat to which they have been subjected, which resulted in the volatilization of the oily matter. When this took place ages ago, if the heat was not so great as to decompose the bitumen in the soft coal; it was expelled and found its way into layers of sand or other places where it is obtained today as *rock oil* or *petroleum*. Occasionally it is under so great a pressure that when opened up it shoots far above the surface in a "gusher." More often it must be pumped from the well. Fig 37 shows a number of oil derricks with the customary pumps.

10. **By-products of Petroleum.**—Petroleum is a black or brownish oil of varying density and viscosity, com-

posed of a great variety of carbon compounds. When dark in color it is because of particles of free carbon contained. There are two general classes of these oils: *paraffin-base* and *asphalt-base.* These names are given for the reason that in the former the thick, less volatile portion of the oil is paraffin, while in the latter it is asphaltum. The paraffin oils are regarded as the more desirable, for the reason that they give on distillation a higher percentage of refined products. The asphalt oils are regarded by some as of animal origin, instead of veg-

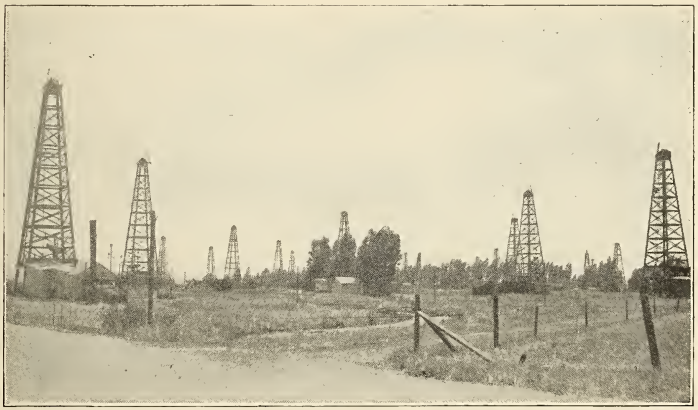


Fig. 37.—Oil derricks, a familiar sight in oil-producing sections.

etable, but produced in the same way. When petroleum is heated in retorts, the low boiling oils distill over first. The process is spoken of as *fractional distillation,* because of the fact that certain portions or *fractions* coming over at a given temperature are separated from other fractions obtained at a different temperature. Below 150° C. the fraction distilling out is called *gasoline;* 150° to 300°, *kerosene;* then successive fractions of heavy burning oil, paraffin oil, lubricating oil, vaseline, and paraffin. After the

volatile products are all off from the paraffin oils a considerable quantity of petroleum coke remains, light and porous, which forms a very excellent fuel. These various fractions may be still further subdivided if desired. Gasoline may, by taking the portions coming off at smaller intervals, be fractionated into *petroleum ether, rhigoline, benzine, naphtha* and *gasoline*. In fact, it is said that some of the refining companies make over one hundred products in distilling paraffin-base oils. At present the demand made by motor cars and other machines using gas engines is mostly for gasoline. Unfortunately, the percentage of this in crude oil is not high. Of late years the great problem has been to devise some way of converting the heavier portions of the oils into the lighter. This is called "cracking" and various plans have been suggested, some of which are fairly successful. Thus a very considerable amount of gasoline, although not present originally in the oil, may be obtained from most good varieties of petroleum.

11. **Natural Gas.**—If sawdust or powdered soft coal is put into a test tube and heated, not merely is there an oily substance, having the odor of tar, driven off, but gaseous products as well, which are combustible. So, in the earth when the buried forests were being subjected to heat, these gaseous products were expelled. Probably vast quantities escaped and were lost; other portions were caught beneath impervious layers of rock and furnish the natural gas of today. Some of it may be due to the chemical action of water upon carbides that were formed, but this will be considered at another time.

12. **Charcoal.**—Formerly charcoal was made in the characteristic wasteful American way. Great piles of wood were covered with earth and sod with several

openings at the bottom to allow the entrance of air. The wood was then set on fire and the lower portions in burning expelled the volatile products from the upper portion, forming charcoal. At the present time, with our rapidly disappearing forests, the wood in suitable lengths is put into iron retorts and heated from beneath by means of coal. By this plan not only is a cheaper fuel used, but various valuable by-products, such as wood alcohol, acetone and acetic acid are saved, with a value probably as great as that of the charcoal itself. There is great demand also for boneblack, a charcoal made from bones. During the last year of the war there was urgent need also for all the nut charcoal obtainable. This is made from cocoanut shells, and all other nuts, even from the pits of the peach, apricot and other similar fruits. This variety of charcoal is by far the most absorptive of any and was used in making gas masks.

13. **Uses for Charcoal.**—Besides the special temporary use of nut charcoal just mentioned, it has some use at all times in research chemical laboratories in absorbing and separating small quantities of rare gases such as those found in the air belonging to the argon group. Boneblack of all the charcoals is probably the most extensively used. Its chief value is in refining sugar. The syrup, brown in color, is passed through charcoal filters whereby the color is removed. A special form of boneblack, known as *ivory black,* made from the horns and tusks of animals, is used considerably as a black paint. Wood charcoal is sometimes used as a fuel in open fires; also in filters for cisterns in suburban and country homes. If so used it should be removed at intervals, and heated to redness to destroy any organic matter collected within the pores. By doing this it is again fit for service. For water in a cistern already contaminated a bag of char-

coal suspended in the water for a few days is sometimes helpful.

14. **Lamp Black.**—This is a finely divided form of carbon obtained by burning in a limited supply of air some oil or gas containing carbon and hydrogen. The hydrogen burns, but most of the carbon is deposited as a soot. It is the best black paint known when ground in oil. It is also the main ingredient of printers' ink.

15. **Coke.**—Coke is made by heating coal in iron retorts, as described for making charcoal, or in specially constructed ovens. When prepared in retorts the volatile products are saved and utilized as will be described later: from ovens the volatile gases are often allowed to escape thus involving great financial loss, as fully one-fourth the fuel value is contained in the volatile portions. Coke is a dark, or steel-gray, porous solid, which burns with intense heat. It is used in iron and other smelters because of its fuel and reducing values.

16. **Gas Carbon.**—On the interior of retorts used in making coke a fine-grained form of carbon is slowly deposited. At intervals this is removed, molded into sticks and plates, and used in arc lights, battery plates and similar other electrical work.

17. **Carbon Monoxide.**—Carbon forms two oxides, the monoxide, CO, and the dioxide, $CO_2$. The latter is always produced in the combustion of carbon when the supply of oxygen is plentiful; when insufficient the former is the result. Little thought is usually given to the lower oxide, but on account of its poisonous properties it demands a very careful study. It may find access to the home in various ways. Most modern houses are heated by hot-air furnaces, usually made of cast iron. Fig. 38 shows the construction. The air enters freely through the ash-pit and in the lower portions of the

firebox carbon dioxide is produced. As this passes up through the layers of red-hot carbon, where there is no air, carbon monoxide is formed, thus,

$$CO_2 + C \rightarrow 2CO.$$

Then as the monoxide flows into the space above the fire it again meets oxygen entering through the drafts and about the door. Hence, it burns and forms carbon dioxide again, thus,

$$2CO + O_2 \rightarrow 2CO_2.$$

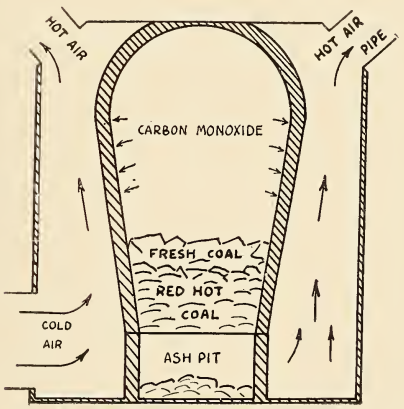



Fig. 38.—Formation of carbon monoxide in a furnace.

The flickering blue flames of burning carbon monoxide may plainly be seen in a furnace into which no coal has been thrown for some time. Likewise, most of the time it may be seen in base burners which use hard coal. Under conditions, as just described, no carbon monoxide remains and the products of combustion are carried out through the flue to the air. There are times, however, when this is not true. At night, in banking the fire so that it will keep well till morning, usually con-

siderable coal is put into the firebox. Now, when the carbon monoxide formed in the interior of the fire reaches the open space, it has been cooled by the layer of coal on top to such an extent that it does not burn. It is then occluded or absorbed by the hot iron of the furnace as is hydrogen by platinum or palladium. Quickly it passes through to the air space about the furnace and is carried by the ascending currents into the living rooms above. The same thing occurs with base burners when the coal is shaken down in considerable quantities from the reservoir above. Gas heaters, when improperly regulated, as may be known by the flame being yellow, often produce carbon monoxide, and tobacco smoke always contains a considerable quantity of the poisonous gas. In lighting with gas, if the mantle is being blackened by a deposit of soot, carbon monoxide is invariably being formed; a cook stove, burning with a yellow flame, is not receiving sufficient air for perfect combustion, and in all probability is producing some carbon monoxide. The burned gases from a motor car or other similar gas engine, especially if the engine is running "idle," contain considerable quantities of carbon monoxide.

18. **Characteristics of Carbon Monoxide.**—It is a colorless gas, of nearly the same density as air. It has a peculiar, somewhat disagreeable but very faint odor. It may be liquefied at −190° C. It burns with a pale blue flame, producing carbon dioxide. From this fact, that it is able to take up more oxygen, it is a reducing agent and often serves thus in the separation of metals from their oxides. This is notably the case with iron, shown by the equation,

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2.$$

Carbon monoxide is very poisonous. When inhaled it forms a compound with the hemoglobin which prevents the carrying of oxygen to the tissues. Thus even in moderate amounts, it causes serious results, asphyxiation and death. Most fatalities reported from asphyxiation by the exhaust from motor cars in a closed garage are due to the poisonous effects of carbon monoxide. Years ago, in the warmer countries of Europe, open charcoal fires were the common method of heating the homes, and many cases of death, accidental or otherwise, are on record due to putting considerable charcoal on top of the fire and retiring. Knowing the poisonous character of the gas no one should sleep in a room warmed by a furnace with the register left open, and even thus, the windows should be raised. In the case of other sources of the gas, as already mentioned, steps should be taken at once to remove the cause. Following explosions in coal mines, quantities of carbon monoxide exist, called by the miners "after damp" or "black damp." Usually it is the cause of the greater number of fatalities.

19. **Carbon Dioxide.**—This gas has already been mentioned as a constituent of the air. It results from the decomposition of organic matter, from combustion and from respiration. All of these sources furnish very considerable amounts, but the proportion of three or four parts per ten thousand of air remains practically constant, due to the action of plant life.

20. **Preparation.**—Carbon dioxide in the laboratory or for commercial purposes is usually obtained by the reaction of some carbonate, as limestone or marble, with an acid, generally hydrochloric. The equation is

$$CaCO_3 + 2HCl \rightarrow CO_2 + H_2O + CaCl_2.$$

It may be collected either by downward displacement or over water; for commerce it is compressed in steel cylinders.

21. **Characteristics.**—Carbon dioxide is a colorless, odorless gas with a density about once and a half that of the air. This may be shown by pouring the gas from a wide-mouthed liter bottle into the upper end of a trough in which are some short burning candles as shown in Fig. 39. The gas cannot be seen, but one candle after another is extinguished as the carbon dioxide flows down. A liter bottle is usually sufficient to make the experiment three times in succession. The gas

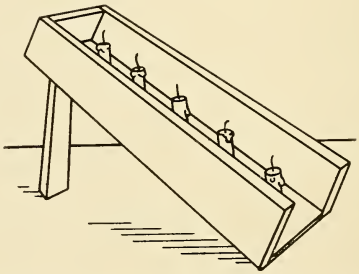


Fig. 39.—Pouring carbon dioxide upon burning candles in a trough.

is soluble in water, about volume for volume at ordinary temperatures. At –79° C. it may be liquefied; if the liquid be allowed to escape rapidly, the lowering of temperature caused by the evaporation converts a considerable amount of the liquid into a white solid, resembling snow, which vaporizes without melting, just as iodine crystals do. Mixed with ether, solid carbon dioxide is often used as a freezing mixture; with it mercury may be easily solidified and many other interesting experiments performed. Carbon dioxide will not burn and is so stable that with very few exceptions it cannot

be decomposed by a burning metal. Magnesium ribbon, ignited and thrust into a bottle of the gas, continues to burn with the formation of magnesium oxide and free carbon. Both products, being solids, may be seen upon the sides of the bottle. The equation illustrating the action is

$$2Mg + CO_2 \rightarrow C + 2MgO.$$

When dissolved in water some portion of the gas reacts chemically, forming a weak and unstable acid, thus,

$$CO_2 + H_2O \rightleftarrows H_2CO_3.$$

Under pressure, carbon dioxide obeys Henry's law, that the amount of *gas dissolved by a liquid is proportional to the pressure.* That is, at five atmospheres' pressure a liter of water would dissolve five times as much gas as at one atmosphere.

22. **Uses.**—The purpose of the small amount of carbon dioxide in the air has already been mentioned. Soda water, so called, is familiar to all. It is water charged with the gas under two or three atmospheres' pressure; as soon as this is relieved the gas begins to escape with the familiar effervescence. Most soft drinks in bottled form are thus carbonated. Carbon dioxide, liquefied in tiny steel capsules, called "sparklets," may be had from the supply houses. They are to be used for the carbonation of water either at home or in camp; for this a specially designed apparatus is necessary, which allows the escape of the gas into the bottle of water by piercing the cap with a stiff needle. Two sizes are made, sufficient for the carbonation of a pint or a quart of water. The chemical fire extinguisher, seen often in the hallways of public buildings, and larger sizes upon fire trucks, makes use of carbon dioxide. Fig. 40 gives a sectional view. Water is put into the vessel, made of

copper or brass, up to the shoulder; in this a pound or a pound and a half of baking soda is dissolved. In the tank near the top supported in a wire frame is a bottle partially filled with sulphuric acid. The stopper of this bottle fits very loosely so that it readily drops out if inverted. For use the whole apparatus is turned upside down; the acid flows out into the soda solution, and reacting with the bicarbonate generates carbon dioxide

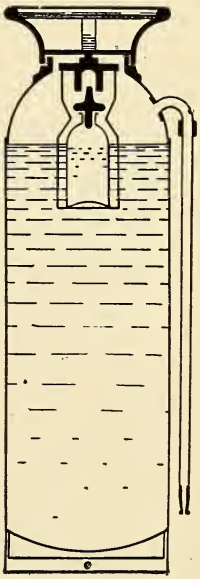


Fig. 40.—Babcock fire extinguisher.

rapidly: the pressure thus obtained throws the water charged with gas upon the fire. The reaction is shown by the equation,

$$NaHCO_3 + H_2SO_4 \rightarrow CO_2 + H_2O + NaHSO_4.$$

The effect of carbon dioxide may be illustrated by a little experiment upon the lecture table. A small evap-

orating dish partly filled with gasoline is ignited; it may be instantly extinguished by pouring carbon dioxide from a wide mouthed liter bottle. Usually a liter of gas is sufficient to repeat the experiment twice.

23. **The Test for Carbon Dioxide.**—On account of its density carbon dioxide often collects in old, long-unused wells and shafts. Although it is not poisonous, one may drown in it as quickly as in water. It is necessary, therefore, to test the air before entering places where it may have accumulated. This may be done by lowering a lantern: if it continues to burn well, the air is safe to breathe. In the laboratory carbon dioxide is tested by bubbling it into lime water, with which it forms a milky white precipitate. If the operation be long continued the precipitate redissolves, thus,

$$Ca(HO)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$

The white precipitate is calcium carbonate

$$CaCO_3 + H_2O + CO_2 \rightarrow CaH_2(CO_3)_2.$$

The product formed by the continued action is acid calcium carbonate which is soluble in water, hence the explanation of the disappearance of the precipitate.

24. **Other Carbon Compounds.**—Carbon tetrachloride, as the name would indicate, has the formula, $CCl_4$. It is a slightly yellow, oily liquid, heavier than water, not inflammable, an excellent solvent for oils and grease, and at present not very expensive. It may, therefore, be used instead of gasoline with perfect safety for cleaning garments. "Carbona," a largely advertised cleaning compound, is mostly carbon tetrachloride. While it contains some benzine there is not sufficient quantity to render the mixture inflammable. "Pyrene," a well-known fire extinguisher, frequently carried by motor car owners in small cylinders, is largely carbon tetra-

chloride. It is readily vaporized, and as the gas is heavy and not inflammable it extinguishes the fire by shutting off the oxygen supply. Silicon carbide, SiC, made by fusing in an electric furnace a mixture of sand and coke with common salt, is a crystalline solid of a dark gray or purple color. The reaction is shown thus,

$$SiO_2 + 3C \rightarrow 2CO + SiC.$$

The compound is said to be even a shade harder than the diamond and is used extensively under the name, *carborundum*, as an abrasive. It is made into whetstones, wheels, and a great variety of other forms for cutting and polishing. Another very valuable carbide is made by fusing in an electric furnace a mixture of lime and coke, thus,

$$CaO + 3C \rightarrow CaC_2 + CO.$$

It is known as calcium carbide and is used extensively as mentioned elsewhere for the preparation of acetylene.

### Exercises for Review

1. What can you say of the importance and total quantity of carbon in nature? Name some of the many forms in which it occurs, as compounds.
2. Classify the forms of carbon.
3. Give proof that the diamond is carbon.
4. Give an account of Moissan's experiment in making diamonds.
5. Give the chief characteristics and practical uses of the diamond.
6. Compare graphite with diamond. Give several important uses.
7. Classify the coals. What is their origin? Why so different?
8. What is the origin of petroleum? Name two kinds. Why so called?
9. What is fractional distillation? What use is made of it? What is meant by "cracking" an oil?
10. Name some of the valuable products obtained from petroleum.
11. What is the probable origin of natural gas?
12. How is charcoal made and what by-products are obtained?

13. Name several varieties of charcoal and give uses of each.

14. What is ivory black? Lamp black? Uses of each?

15. How is coke prepared? Its chief uses?

16. What is the source of gas carbon? What uses has it?

17. Name several ways in which carbon monoxide may find its way into the home. Give the details of one case.

18. Describe carbon monoxide. Its effects upon the blood.

19. Give the sources of carbon dioxide in the air.

20. How is carbon dioxide made for commerce? Equation.

21. Give chief properties of carbon dioxide.

22. Name some important uses for carbon dioxide.

23. Describe the chemical fire extinguisher. Give the chemical reaction.

24. Give two tests for carbon dioxide.

25. What valuable uses has carbon tetrachloride? Name some commercial forms in which it appears.

26. Name two carbides, state how made and uses of them.

## CHAPTER XIII

## VALENCE

**Outline—**

Meaning of Valence
Degrees of Valence
Valence of Radicals
Variation of Valence
    Saturated and Unsaturated Compounds
Valence in Ternary Compounds

1. **Meaning of Term.**—As used in chemistry the term valence means the *power* an atom has of combining with one atomic weight of hydrogen or its equivalent. Thus, in hydrogen chloride, one atomic weight of chlorine combines with one of hydrogen. As the hydrogen atom serves as the unit, chlorine must have a valence of one; likewise, do bromine, fluorine and iodine. Radicals, not being compounds but groups serving like atoms, as parts of a compound, likewise have valence. Thus, chloric acid, $HClO_3$, shows that the group $-ClO_3$ has a valence of one; so, also, ammonium, $NH_4-$, in ammonium chloride; $-NO_3$ in nitric acid; $-HO$ in sodium hydroxide and several others. As the metals are electropositive and do not form any familiar compounds with hydrogen, their valence must be determined by examining some such compound as their chlorides. Thus, common salt, NaCl, shows that sodium has a valence of one; KCl, that potassium has a valence of one. All atoms or groups having a valence of one are said to be *univalent* or are sometimes called *monads.*

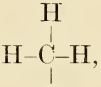
2. **Valence Greater than One.**—If we examine the formula for the water molecule, we see that oxygen has combined with two atoms of hydrogen, hence oxygen is

said to have a valence of two. Similarly, magnesium as seen in magnesium oxide, MgO, copper in copper oxide, CuO, calcium in lime, CaO, all have a valence of two and are called *bivalent* or *diads.* Aluminum and iron as shown by the formulas, $AlCl_3$ and $FeCl_3$, are *trivalent* or *triads;* while carbon, as seen in carbon dioxide or carbon tetrachloride, and silicon in silicon dioxide, $SiO_2$, are *tetrads* or *quadrivalent.* Phosphorus as seen in the compounds $P_2O_5$ and arsenic in $As_2O_5$ are *pentads.*

3. **Radicals of Valence Higher than One.**—In sulphuric acid, $H_2SO_4$, sodium carbonate, $Na_2CO_3$, and potassium chromate, $K_2CrO_4$, are seen radicals combining with two univalent atoms; hence, $-SO_4$, $-CrO_4$ and $-CO_3$ must be bivalent. Likewise, $-PO_4$ and $-BO_3$, seen in the phosphoric and boric acids, $H_3PO_4$ and $H_3BO_3$, are trivalent; while $-SiO_4$ found in orthosilicic acid, $H_4SiO_4$, is quadrivalent.

4. **Variation in Valence.**—Nitrogen and phosphorus are spoken of above as being quinquivalent. Their oxides indicate this. But they also form the hydrogen compounds, ammonia, $NH_3$, and phosphine, $PH_3$, in which a valence of three is indicated. In another chapter, copper is seen to form two compounds, as also mercury, CuO and $Cu_2O$, $HgCl_2$ and $Hg_2Cl_2$, indicating sometimes a valence of one, sometimes of two. Many other cases might be cited, notably carbon in carbon monoxide and the dioxide, also marsh gas, $CH_4$, and ethylene, $C_2H_4$. In the case of the carbon atom the valence is universally regarded as four and such compounds as ethylene, $C_2H_4$, acetylene, $C_2H_2$, and the monoxide are said to be *unsaturated.* By this is meant that the carbon atom in such compounds has not combined with all that it is capable of holding. There is abundant evidence that this is true. We have seen already in the case of the

carbon monoxide that it readily combines with another atom of oxygen forming the dioxide; also, that inhaled it completes the saturation by combining with the hemoglobin of the blood; likewise, it readily unites with two atoms of chlorine to form phosgene, $COCl_2$. Other very remarkable and interesting proofs for the carbon compounds are abundant. One of these is the passage of the gas through a solution of bromine in water or through a quantity of bromine beneath a layer of water to prevent its escape into the air. Marsh gas, $CH_4$, if carbon has a valence of four, would be a saturated compound. When it is slowly bubbled through bromine, no matter how long continued, the escaping gas has all the properties of marsh gas and the bromine remains unchanged. On the other hand, if ethylene, $C_2H_4$, be used in the same way, the bubbles in passing through seem to become smaller as if they were being absorbed, and after an hour or two, the red color of the bromine has entirely disappeared, and in its place is a colorless, oily liquid, of pleasant odor, without the slightest resemblance to bromine. An analysis of this liquid shows that it contains two atomic weights of bromine per molecule, as would be represented by the formula, $C_2H_4Br_2$. If written graphically, which shows the structure or arrangement, marsh gas is



, ethylene,

, and the bromine compound,

. These formulas show that in marsh gas, the carbon atom has all its bonds saturated with hydrogen: that in ethylene there are two not so used and it is to

these that the bromine has been attached. A very large number of other similar experiments have been made, all of which seem to show the truth of the position taken. Likewise, in the case of most of the seeming variations in valence, one or more of the compounds are unsaturated ones. Thus nitrogen in ammonia, $NH_3$, seems to have a valence of three; but ammonia readily forms additional compounds, as when it is brought into contact with hydrochloric acid, thus,

$$NH_3 + HCl \rightarrow NH_4Cl.$$

In the last compound the nitrogen atom is combined with five univalent atoms. Likewise, ammonia combines additively with nitric acid,

$$NH_3 + HNO_3 \rightarrow NH_4NO_3,$$

in which compound the nitrogen atom is combined with four univalent atoms and one univalent group. Mercury in mercurous chloride, $Hg_2Cl_2$ has apparently a valence of one, while in mercuric chloride, $HgCl_2$, it is evidently two. In all probability the mercury atom always has a valence of two, and any compounds not indicating such are unsaturated. It is well known that mercurous salts readily take up more of an electronegative element or group and become mercuric compounds. Thus, many other cases might be considered but for the present these seem sufficient.

5. **Ternary Compounds.**—Sometimes it becomes desirable to determine the valence of an element in a compound, knowing the formula. In binary compounds, if the valence of one of the elements is known, the other is evident at a glance. In ternary compounds this is not true. However, if it is known that the valence of the oxygen atoms is equivalent to the added valences of the other atoms present, it becomes easy. To illus-

trate, sulphuric acid has the formula, $H_2SO_4$. It is desired to know the valence of the sulphur atom in the compound. There are four oxygen atoms whose total valence is 8; the two hydrogen atoms have a valence of 2; hence, $2 + S = 8$, from which sulphur must be 6. In potassium dichromate, $K_2Cr_2O_7$, the equation, $2 + 2Cr = 14$, indicates the several valences, from which chromium is found to be six.

### Exercises for Review

1. Define and illustrate valence.
2. Name some elements with a valence of one; some radicals with the same valence.
3. Name some elements with valence of two; also some radicals.
4. What names are given to elements with valence of one, two, three, etc.?
5. What is meant by an unsaturated compound? Name two.
6. Give some experimental proof that ethylene is unsaturated.
7. What facts indicate that carbon monoxide is unsaturated?
8. What is a structural or graphic formula? What advantage has it?
9. What evidence is there that ammonia is unsaturated?
10. Find the valence of chromium in $K_2CrO_4$; nitrogen in $HNO_3$; manganese in $KMnO_4$; iron in $Fe_2O_3$; phosphorus in $P_2O_5$; phosphorus in $H_3PO_4$.

## CHAPTER XIV

## ILLUMINATING AND FUEL GASES

**Outline—**

Natural Gas
Acetylene
Pintsch Gas
Blau Gas
Coal Gas
Water Gas

1. **Natural Gas.**—This has already been mentioned and its supposed origin. Another theory has been suggested by some which may possibly account for at least a part of the natural supply. Two carbides have been mentioned in the preceding chapter. One of them reacts with water, as will be seen, to form a combustible gas. Another, aluminum carbide, does likewise. It is thought that at some time in the past this carbide has been formed in the earth and that water coming in contact with it reacts forming marsh gas, which is the main constituent of natural gas. The reaction with water is here shown,

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 2Al_2(HO)_6.$$

2. **Acetylene.**—For commercial purposes, acetylene is always prepared by the reaction of water upon calcium carbide, thus,

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(HO)_2.$$

Owing to the high percentage of carbon in the gas, it cannot be used in an ordinary burner, for the insufficient amount of air supplied results in a very smoky flame. A special tip, shown in Fig. 41, is designed so

as to draw in the air by two minute jets of gas directed toward each other. Burned thus, a brilliant white light is obtained with only about one-fifth the quantity of gas consumed as in other common burners. It is thus used extensively in motor cycles: for this purpose it is contained in the familiar "Prestolite" tank. At first, attempts were made to use acetylene in liquefied form, but it was found under such pressures to be readily explosive and many accidents occurred. It is very soluble in acetone, a liquid of pleasing odor obtained in the destructive distillation of wood in making charcoal. The prestolite tank applies this principle: large quan-

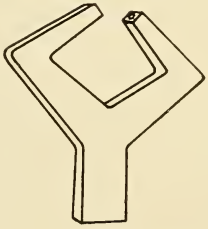


Fig. 41.—Acetylene burner.

tities of acetylene under several atmospheres pressure are dissolved in the acetone in the tank and in this form it is perfectly safe. On use the gas escapes, but the acetone remains and may be recharged. For cooking purposes special plans must be had for furnishing increased quantities of air, otherwise the cooking vessels become heavily coated with soot. At the present time acetylene is used extensively in country churches and suburban homes both for lighting and cooking. There are several types of generators, but the most satisfactory is one in which the carbide in coarse grains drops slowly into a considerable quantity of water. The gas

is piped throughout the house in the usual way and burned in tips like the one described above. The most valuable use of acetylene at the present time is for welding and similar work where great heat is required. The gas is used in a torch such as was described for oxy-hydrogen work, and when properly adjusted burns with a pale blue, intensely hot flame. Even when air instead of oxygen is used, furnished with a foot bellows, iron wire, such as is used in baling hay, may be burned rapidly in the air with a beautiful and dazzling shower of sparks. In welding, the broken object is heated, the crack made somewhat larger; then a rod of steel is melted in the oxyacetylene flame and the molten steel allowed to flow down into the crack. Welding thus properly done is said to make the object as strong as at the beginning.

3. **Pintsch Gas.**—This gas received its name from an Englishman who first prepared it for the purpose of lighting the stage coaches of that day. At the present time it is used practically nowhere outside railway coaches, where it is seen in clusters, usually enclosed in glass globes at the ceiling. It is prepared from some oil, often naphtha, by heating sufficiently high to decompose it into gases which will not liquefy again upon cooling. As it is thus made from a refined oil, the resulting gas needs little purification, other than the removal of a little tar and water. It is carried, heavily compressed, in cylinders under the railway coaches. Unlike most similar gases, the compression does not greatly reduce its illuminating powers.

4. **Blau Gas.**—At the present time a similar gas, called Blau gas, is being manufactured from a less refined oil than the pintsch uses. It is purified and compressed, whereupon some of the constituents become liquid.

These are removed and the gas is then stored in steel cylinders under high pressure. In the oxyhydrogen blowpipe it gives intense heat; it is also used in suburban homes for cooking and lighting purposes as other gases are in the city. For such use two tanks of the compressed gas are placed in a container outside the building and attached to the piping of the house. When one is exhausted it is sent to the factory for refilling and the other put in service.

5. **Coal Gas.**—Most cities in sections where bituminous coals are to be had, use large quantities of coal gas. It is prepared by heating the soft coal in iron retorts as already mentioned for making coke. The resulting gaseous mixture, very impure, must be purified before being suitable for use. By cooling, first the tar is removed and flows into a tank or well fitted to receive it. The gas next passes through, usually, two "towers," filled with lumps of coke or something equivalent, kept moist by water trickling over it. Here the ammonia is removed. The gas next passes through three or four purifiers, containing lime or ferric oxide, which remove other compounds like sulphur dioxide, hydrogen sulphide and carbon dioxide, all acidic in character and either not combustible or very undesirable in an illuminating gas. Finally, the gas is metered and passed into a storage tank from which it is piped to all parts of the city. Remembering that coke and gas carbon are both obtained in the retorts it will be seen that there are four by-products of the manufacture of coal gas. Besides the two just named, are the tar and ammonia. Tar is a black, viscous, ill-smelling liquid consisting of a mixture of a great variety of compounds and black because of the presence of some free carbon. From it are made several colorless liquids, such as

aniline and toluol. These form the basis of an indefinite number of other compounds of the very greatest value: photographic developers, such as hydroquinon; many medicines, like aspirin; all the great variety of beautiful aniline dyes; phenol or carbolic acid and its many derivatives; picric acid and the explosives from it; the explosives from toluol, and hundreds of others.

A ton of coal will make about ten thousand cubic feet of gas containing one-fourth to one-third the fuel value of the original coal. The gas consists of hydrogen and marsh gas, over 40 per cent of each, with carbon monoxide, and ethylene as the greater part of the balance. Small proportions of some higher hydrocarbons are usually present.

6. **Water Gas.**—This receives its name from the fact that steam is used in its preparation. Often both coal and water gas are manufactured simultaneously in the same building. The coke obtained as a by-product in the coal gas department is withdrawn red-hot from the retorts into small steel cars in which it is carried quickly to another part of the building. Here it is dumped through a trap door into a vertical, cylindrical retort on the floor below. A blast of air is turned on the hot coke to raise its temperature, and then live steam is passed through it, when the following reaction takes place,

$$H_2O + C \rightarrow H_2 + CO.$$

At the end of about three minutes the temperature is too low to effect the decomposition of the steam, which then, automatically, is cut off and the air again turned on. Thus, in three minute periods, mechanically, all day the steam and air are turned on alternately, with results as shown by the equation. Both the constituents thus obtained are combustible, but a gas richer in

carbon is more desirable. Hence, it is passed through another retort containing a lattice work of fire brick heated to redness by a gaseous fuel. Into this chamber is sprayed an oil obtained from petroleum, which is decomposed as was described in making pintsch gas. These products are mixed with the two already obtained from the steam and coke, such that the final result is not essentially different from coal gas. The percentage of carbon monoxide is higher, hence the gas is more poisonous. In factories making both coal and water gas the large storage tank receives both usually in something like the proportion of 3 of water to two of coal gas. In other cities where cheap supplies of soft coal are not available, as in California, a gas is prepared from crude petroleum, not essentially different from the coal gas, and of excellent quality.

### Exercises for Review

1. Give a chemical theory for the formation of natural gas. Of what does natural gas consist?

2. How is acetylene made? Write the equation. Describe the tip necessary for burning it successfully.

3. Describe the prestolite system of lighting.

4. Why not use liquefied acetylene for lighting?

5. Give some important uses of acetylene.

6. How is pintsch gas made? Where is it used?

7. How is blau gas made? For what used?

8. Describe the process of making coal gas. Name the impurities removed in its manufacture; also the by-products obtained.

9. How is the ammonia recovered and purified?

10. What are some of the products obtained from tar?

11. What are gas carbon and coke used for?

12. Describe the preparation of water gas. Why is it so called?

13. How is the composition of water gas different from that of coal gas?

14. Write the equation showing the effect of the hot coke on the steam.

15. What is meant by "live" steam?

# CHAPTER XV

## FLAME

**Outline—**

Definition of Flame
Chemical Reaction in a Flame
Structure of Flames
The Bunsen Burner
Applications in the Home
The Oxyhydrogen Blowpipe
The Blast Lamp

1. **What is a Flame?**—Briefly stated, a flame is usually said to be a burning gas. It is the phenomenon which accompanies the rapid union of two gases, producing heat and usually light also. At first thought this might not seem to be always true. In the case of a burning gas jet there could be no question about it. The gas, being heated to the kindling temperature, begins to combine with the oxygen of the air; this chemical union is productive of heat and a temperature above that necessary for the kindling of the gas is constantly maintained. With a candle it is equally true. The wick is filled with wax. When a burning match is applied to it, first the wax is melted, then it begins to vaporize and the gas thus formed is ignited. Thereafter, the heat of the chemical union is such as to vaporize continuously the paraffin with a steady flow of gas. By quickly blowing out the flame of the candle, the paraffin vapors may be seen floating upward and may easily be ignited without touching the wick. When this is done the flame rapidly passes down the stream of gas to the wick. Exactly the same thing is true of the kerosene or alcohol lamp. Likewise, when wood is burning the heat of

combustion decomposes the cellulose and other compounds present, converting much of them into gaseous form. These escape in tiny streams here and there and combining with the oxygen produce flames. It is the same with soft coal. The oil contained, by means of the kindling used, is first partially volatilized; later, by the heat of combustion not only does volatilization continue but also decomposition of the vapors into hydrocarbon gases, all of which are combustible. Charcoal, coke and anthracite coal contain little or no volatile matter; hence, they burn without flame. It is true that often light blue lambent flames may be seen above the surface of such fires, but these are due to the carbon monoxide, produced in the interior of the burning mass through the interaction of the carbon dioxide and red-hot carbon. This has been explained elsewhere. It must be concluded, therefore, that whenever there is flame, there is a gas present.

2. **The Chemical Action.**—Combustion is sometimes spoken of as the rapid union of *oxygen* and some other substance. This is a narrow view. A flame may accompany the union of a variety of substances, and in each particular case, one of the substances is as essential as the other. For example, an ignited jet of hydrogen, thrust into a bottle of chlorine, continues to burn as vigorously as in the air. Likewise, if an inverted bottle of hydrogen be ignited at the mouth and a jet of chlorine be introduced through the flame into the bottle, the chlorine will be seen to burn. In this case combustion is the rapid union of the hydrogen and chlorine, and it makes little difference which is introduced into the other; one is just as essential as the other. In the same way a stream of air, or oxygen, passed through the flame into the bottle of hydrogen continues to burn just as well as the jet of

hydrogen does in the air. This is illustrated by a common, simple experiment. The smaller tube in Fig. 42, marked "gas," is attached to the gas supply. The larger, short tube is open to the air. When the gas has been flowing sufficiently long to expel all the air a small flame brought to the upper end of the "air" tube will apparently ignite the air current and it will continue to burn. Here the combustion is the union of the gas and oxygen and the flame occurs at the place where this union is going on.

Fig. 42.—"Burning" air.

3. **Structure of a Flame.**—The ordinary flame of which that given by a candle is typical consists of three portions, or concentric cones. A few simple experiments readily enable one to determine the condition of each of these portions. A pine splint held across the flame of a large candle, or more conveniently, a small Bunsen burner flame, will be scorched in two places, at the points where it intersects with the circumference of the flame. If a sheet of paper be pressed down upon a small Bunsen flame, or better, if the burner be inverted and held close to the paper lying on the table, it will be scorched in a circle, agreeing with the circumference of the flame. These would indicate that the burn-

ing portion of the flame is at the outer edge. To show this more strongly, a match may be thrust through the outer zone and held until the wood begins to burn at the circumference of the flame without the more combustible material of the head of the match being ignited at all. This may be varied by turning off the gas and suspending a match in the burner by means of a pin thrust through the wood a half inch or so from the head. If now the gas is turned on and ignited at some distance above the tip, it will burn as usual while the match remains unaffected at the center. These experiments

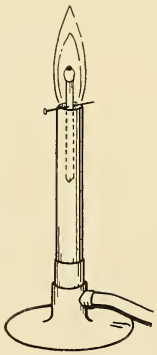


Fig. 43.—Match suspended within burning gas jet.

show that there is no heat in this innermost cone; lastly, a small tube inserted into this section and held at an angle, may be lit at the upper end. This shows that this portion contains unburned gas. The same experiments may be carried out with a large candle. (See Fig. 44.)

Inspection of a Bunsen flame with the openings near the bottom closed or of the candle flame shows that the middle cone is yellow. Around this is an outer blue cone, very thin at the base, much larger in the upper part. A cold dish held against the yellow portion is

soon covered with soot which we know is a deposit of carbon. It is the myriads of carbon particles floating in this zone and heated to incandescence, that is to a temperature at which they will glow, which give the light. It may be concluded then that this middle cone consists of gas undergoing combustion but not completed and contains much incandescent carbon. The outer cone gives little or no light. In the daytime it looks much smaller than it really is. A pine splint ap-

Fig. 44.—Burning gas drawn from center of candle flame.

proached slowly from above or from the side ignites long before it touches any visible flame. This is evidently the hot portion and is the zone of complete or perfect combustion: In it the carbon is burned to carbon dioxide and the hydrogen to vapor. Obviously, if heat is desired as in softening a glass rod, it will be secured in the upper, nearly invisible, blue portion of the flame. If *reducing* action is wanted, since red-hot carbon has

such power, it will be had in the yellow cone. A penny held in the tip of the flame becomes black from a coating of copper oxide; held in the yellow portion it becomes bright again because the hot carbon removes the oxygen from the film of oxide.

4. **The Bunsen Burner.**—There are several types of this burner found in laboratories. In all of them the gas enters through a very small opening somewhere near the bottom, and all have some arrangement for introducing considerable air somewhere near where the gas enters, so that the two become mixed before leaving the tube. The result is that if properly adjusted there are only two portions to such a flame. The luminous part has disappeared, while the outer cone is much enlarged. There is thus obtained a hotter flame than is possible otherwise. By opening and closing the air vents at the bottom it will be seen that the flame is much shorter when the air is on than otherwise; hence all the heat of the combustion is concentrated within a shorter portion than when the air is not entering. Sometimes, in such burners, if the gas pressure is low, the burner "strikes back" and continues to burn near the base. In this case the rate of combustion or speed of propagation of the flame has been more rapid than the flow of gas, and the flame is passed down the pipe to the point of exit of the gas. Owing to the lack of air needed for perfect combustion, acetylene and other offensive gases are often produced in such cases and the difficulty should be speedily remedied. Usually by turning off the gas and lessening the air supply the burner may be relit successfully.

5. **Applications in the Home.**—Every gas stove used for cooking and, as a rule, for heating as well, employs the principle of the Bunsen burner. There is some de-

vice for admitting a supply of air and mixing it with the gas before it reaches the burner where it is to be consumed. If properly adjusted, the flame will be blue and relatively hot. A yellow flame indicates that not sufficient air is being provided; hence results will be slow and unsatisfactory. Sometimes the burners on a stove, especially the oven, may strike back and burn at the point of admixture of the gas and air. This is especially apt to occur after the oven has been burning for some time and the pipes have become hot. The cause is the same as in the case of the Bunsen burner. The remedy is to turn off the gas, decrease the air supply and relight. With poor gas pressure there is sometimes no remedy except to allow the pipes to cool.

6. **The Oxyhydrogen Blowpipe.**—This burner has been described elsewhere, under hydrogen. If the flame obtained by this torch or with acetylene be examined, it will be seen to consist of only two portions—a very small inner cone and a nearly invisible outer one. The gases used are so proportioned and so thoroughly mixed before they issue from the tip that the combustion is perfect throughout nearly the entire mass. Further, it will be seen that the flame is relatively a small one. The result is a flame of very great intensity.

7. **The Blast Lamp.**—The construction of the blast lamp is not essentially different from that of the oxyhydrogen torch. The inner pipe is attached either to a foot bellows or to a tank of compressed air, while the outer connects with the gas supply. Before the air is turned on, the gas burns with a large, flickering, yellow flame, with low temperature. With the air, the flame decreases greatly in size, loses its yellow portion, becomes blue and almost invisible, and has a high tem-

perature. The admixture of the air in the tube enables the entire amount of the gas to be consumed within a small space, so that the heat is all concentrated therein.

### Exercises for Review

1. What is a flame? Show that what you say is true of the candle and of a kerosene lamp.

2. Give some experimental proof that a stream of gas is being formed in the candle wick.

3. What is the explanation of the flame above a hard coal fire?

4. Explain combustion in a broad sense. Show how air may be "burned."

5. Of how many portions does an ordinary flame consist?

6. Give some simple experiments to show something as to the character of the innermost part of a flame.

7. What does the middle cone contain? What proof can you give?

8. What is the character of the outer cone? How do you think it would appear different at night from in the daytime?

9. What is meant by incandescence?

10. Describe the Bunsen burner as found on your desk.

11. What effect does the construction of the Bunsen burner have on the structure and character of the flame?

12. Why is the flame shorter when the air is on at the bottom?

13. Explain why a burner strikes back and give the remedy.

14. What applications of the Bunsen burner are found in most city homes?

15. What is the trouble when a gas flame on a cook stove burns yellow? How can it be remedied?

16. Explain why the oxyhydrogen flame is so intense in heat.

17. Describe the construction of the blast lamp. Why is the flame so large before the air is turned on?

## CHAPTER XVI

## METHODS OF LIGHTING

**Outline—**

Primitive Methods of Lighting
Kerosene Lamps
Gas Illumination
Incandescent Electric Lights
The Welsbach System
Tungsten Electric Lamps
The Lime Light
Arc Lights

1. **Primitive Methods of Lighting.**—When man first began to use artificial light is not known. Probably in some localities, at first it was the pine knot full of resin; in others, a bowl of oil into which was dipped a twisted rag or something which served as a wick. Miners, even now, often carry upon their caps a lamp containing a thick oil with a wick enclosed in a tube. Such lights are necessarily poor, more or less unsteady, and productive of smoke. The candle was an improvement upon the old, open oil lamp. At first, tallow was used and later the oil of the sperm whale. Sometimes, even now, for hard candles, tallow is treated with an acid to precipitate the stearic acid from the stearin and this is melted and molded into shape. Those most commonly used, however, are made of paraffin, obtained from petroleum. The light obtained is due, as explained in a preceding chapter, to the presence of the incandescent carbon particles in the flame.

2. **The Kerosene Lamp.**—A decided advancement was made in lighting when the kerosene lamp was invented. The principle is not different from that of the candle.

By capillarity the oil is drawn up through the wick and burned at the top. The chimney is the source of the increased light. By means of the perforations in the support for the chimney at the bottom a draft is secured so that the combustion is more rapid, the carbon particles in the incandescent zone reach a higher temperature and, therefore, give more light. Moreover, the flame is a steady one and produces less smoke. In earlier years there was frequently more or less gasoline

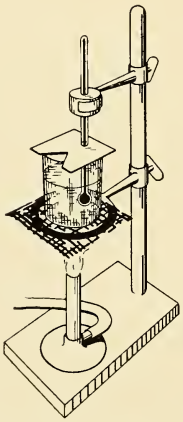


Fig. 45.—Determination of flash point of an oil.

mixed with the kerosene, for at that time there was no demand for the lighter oil. As a result, explosions were not uncommon. This led to legislation requiring all merchantable kerosene to be inspected and possess a certain "flash point." This means the temperature at which the vapor arising from it will ignite. It may be shown fairly well by a very simple method, as seen in Fig. 45. A thermometer is supported on a stand at such a height as to dip within some gasoline or kerosene in a beaker. A piece of cardboard with an opening

cut on one side covers the beaker. The oil is then slowly and cautiously heated with a small flame. At intervals, a small wax taper, lighted, is brought to the opening in the cardboard. The temperature at which the vapor arising catches fire or "flashes" through the space above the oil is called the flash point. At the present time, since gasoline is the valuable product obtained from petroleum, kerosene is always free from the more volatile oil and explosions are almost unknown.

3. **Gas Illumination.**—The next step in artificial lighting was by means of gas, at first made from soft coal. For its combustion a burner was used closed at the top by a little cap made of fire clay or some similar noncombustible material, with a narrow slit for the escape of the gas. When ignited a thin, fan-shaped flame was the result. The light produced was the result of the incandescent carbon particles as in other cases already studied.

4. **Electric Lights.**—The next improvement in lighting systems was that of the incandescent electric bulb. It had long been known that a wire of high resistance carrying an electric current would become luminous. Attempts were made with platinum and other metals in electric lamps, but none of them gave sufficient light to be of value. Finally, after years of experimenting with all sorts of vegetable fibers, one from a special bamboo was obtained sufficiently strong to be used in a lamp. Later, these carbon filaments were obtained by carbonizing threads made from a viscous solution of cellulose, much as fiber silk is now. The air was pumped out of the bulb, so as to prevent the rapid disintegration or combustion of the carbon thread. In such lamps, it will be seen that the light, as in all other cases already mentioned, is obtained by incandescent carbon. Natu-

rally, they were called incandescent lights. The convenience of turning on or off such lamps was great, and the candle power was higher, but the quality of the light otherwise was not essentially different from the gas-light.

5. **The Welsbach Mantle.**—Two things led to the invention of the gas mantle. One was the discovery of natural gas, and the desire to use it for illuminating purposes. As it is low in carbon content, when burned in the old-fashioned slit-top burner, it gives very little light, not sufficient to be of value. The other reason was the greater convenience offered by electricity with the resulting strong competition, threatening to displace gas entirely. At such a time the mantle was invented by a man named Welsbach. It is made by spraying upon a little hood made from long fiber mercerized cotton, a mixture of thorium and cerium nitrates, 99 parts to 1. The burner upon which it is used is almost identically that invented by Bunsen. For use the mantle is hung over the burner and ignited. The cotton burns off, while the two nitrates by the heat are converted into oxides. Now, when the gas is ignited, the burner gives a short, hot flame which heats the two oxides into incandescence just as the oxyhydrogen flame does the stick of lime, which is calcium oxide. At the temperature obtained, the oxides give a beautiful, white light, six or eight times as strong as the old style tip. Natural gas can be used in this burner as well as artificial. The quality of the light is greatly superior to that of the incandescent carbon electric, and not essentially different in candle power.

6. **Acetylene.**—This gas has been mentioned elsewhere although it is used more for illumination than for cooking purposes. It must be burned in a special tip and cannot be used with the Welsbach mantle. It gives a

beautiful white light, but as the gas must be manufactured in the place where it is be used, it is not adapted to the wants of a city. Its field must always be the suburban or country home.

7. **The Tungsten Lamp.**—The quality of the light afforded by the Welsbach gas system stimulated the electric companies to discover some filament which would give a white light comparable with gas. Several substances other than carbon have been tried, but at the present time tungsten is regarded as the most desirable. When first adopted such lamps were very fragile, owing to the brittleness of the filament, and gained slowly in favor. They have been perfected now, however, so that they are practically as durable as the carbon filaments. They give a brilliant white light, and consume much less current for the same candle power than the old style lamp. An improved form of the tungsten lamp now has the bulb filled with nitrogen instead of the usual vacuum. They are more durable and at the same time give a better light. Without accident a tungsten lamp should give about 1,000 hours of actual service.

8. **The Calcium or Lime Light.**—This has been mentioned elsewhere as the Drummond light. The principle is not different from that seen in all other cases and is due to the incandescence of a solid. In this case it is the stick of lime, calcium oxide, upon which an intensely hot flame is allowed to strike. Its brilliance rivals that of the electric arc. Its use has been mentioned elsewhere.

9. **Arc Lights.**—In arc lights two sticks of gas carbon are used which in service are separated from each other by a short distance. An electric current of high voltage, in spanning the gap, does so not in a straight line, but curved like the arc of a circle. The positive carbon

is worn away and the particles, white hot, are carried across the gap and in part deposited upon the negative carbon. It is these white-hot particles which produce the dazzling light. At first the two carbons were used in large globes entirely exposed to the air. As a result they were burned away rapidly, so that a great deal of time was needed in replacing them, in addition to the expense of the carbons themselves. At the present time they are enclosed in small globes. These are not air-tight, but through combustion they are soon filled with carbon dioxide so that the subsequent disintegration is slow. Arc lights are used mainly for lighting of streets, and spot lights for stage effects.

### Exercises for Review

1. Name some of the different kinds of candles made. How is light produced in a candle?

2. Explain why the kerosene lamp gives better light than the candle. Why were they explosive at first?

3. What is meant by the flash point of an oil? How may it be obtained approximately?

4. Describe the tip used in the original gas lamp. What produces the light in such a flame?

5. Describe the incandescent carbon lamp. How are the carbon filaments made now? How originally obtained?

6. What objection to the carbon electric? What advantage has it over gas?

7. Describe the Welsbach mantle and burner. What are its advantages?

8. What kind of a tip is used with acetylene? Where are acetylene lights seen frequently? To what kind of lighting is it essentially suited?

9. How is the tungsten lamp different from the old carbon? What objection was there to them at first?

10. In working about a tungsten lamp, as in dusting or cleaning, what can be done to render them still less liable to break?

11. How is the calcium light obtained? For what is it used?

12. Why are arc lights so named? Where used? What produces the light? Where are the carbons obtained which are used in the arc light?

## CHAPTER XVII

## SOME ORGANIC COMPOUNDS

**Outline—**

Hydrocarbons
- (*a*) Methane
- (*b*) Gasoline and Kerosene
- (*c*) Derivatives of Methane

The Alcohols
- (*a*) Wood Alcohol
- (*b*) Grain Alcohol

Organic Acids
- (*a*) Formic
- (*b*) Acetic

Aldehydes
- Formalin

Ethers

1. **Hydrocarbons.**—It has been stated elsewhere that the study of carbon compounds constitutes a separate branch of chemistry, known as "Organic Chemistry." The compounds were originally so named because, as far as observed, they were produced only by organized life forces. This is known now not to be true. From their very great practical value in everyday life with some of these compounds it is important that the student should become familiarized. Among the simplest of such compounds are the *hydrocarbons,* which contain as the name indicates only carbon and hydrogen. In a preceding chapter marsh gas has been mentioned, as have also gasoline, kerosene and various other oils derived from petroleum. All these are really paraffins and belong to

a regular series in which over sixty have been prepared. The first six are here given,

Methane, $CH_4$,
Ethane, $C_2H_6$,
Propane, $C_3H_8$,
Butane, $C_4H_{10}$,
Pentane, $C_5H_{12}$,
Hexane, $C_6H_{14}$.

The subsequent members of the series receive their names from the Greek numerals as the last two given above, the first part of the name indicating the number of carbon atoms. Examination of the formulas shows that the difference between any two successive members is $CH_2$; hence, it becomes a simple matter to write formulas for the entire series. Further it will be observed that the hydrogen is always twice the carbon plus two. The general formula for any paraffin, therefore, is $C_nH_{2n+2}$ in which $n$ represents the number of the carbon atoms. Of the more than sixty paraffins known, the first five are gases, then follow a very considerable number of liquids, and above these are the solids with which all are familiar in the white wax of commerce.

2. **Methane.**—This is commonly known as marsh gas, because of the fact that it is produced in swamps and stagnant creek beds where decomposition of leaves and other organic matter is taking place. It occurs in coal mines, and is known by the miners as *fire damp,* the word *damp* being their name for gas. It is so called because of its dangerous, explosive character. It is this gas which causes practicallly all the explosions in coal mines. As in such cases the combustion is more or less imperfect from the limited supply of air, much carbon monoxide usually exists in the mine following the explo-

sion. This has been mentioned before as the fatal black damp. It has been mentioned, also, that methane is the chief constituent of natural gas, is more than 40 per cent of coal gas, as well as a very considerable part of water gas. It is colorless, has a density only eight times that of hydrogen or little more than half that of the air, is odorless, and burns with an almost invisible blue flame. On account of its having no odor its presence in mines cannot be detected by the senses. For protection against it, more than a century ago, Sir Humphrey Davy invented a safety lamp which consists really of very little more than a chimney of fine wire gauze, surrounding the flame, like the chimney on a lantern. All it does is to prevent the gas on the outside from becoming heated to its kindling temperature. This will be understood if a wire gauze be held above a burning Bunsen flame. Apparently, it is possible by means of the gauze to push the flame down. Really, however, what it does is to conduct the heat away from the gas and dissipate it so that the gas in passing through is cooled below its kindling point. That this is so may be shown by bringing a flame to the current of the gas above the gauze. It is quickly ignited and goes on burning.

3. **Gasoline and Kerosene.**—Gasoline consists mainly of the sixth, seventh and eighth of the paraffin series, hence is a mixture. Benzine and the other light oils mentioned as belonging to the gasoline fraction obtained from petroleum below 150° C. may be separated from each other by taking smaller fractions. To illustrate, a sample of gasoline may begin to boil at about 75° C.: the petroleum ether comes off first and because it has a very low boiling point it is soon all distilled over. The receiving flask will then be removed and another attached for the next fraction. Kerosene consists of the

eight paraffins just above the gasoline series. Having seen the close relation of the various oils to each other in the paraffin series, it is less difficult to understand how by "cracking" it might be possible to convert the higher members into the lower, since a single molecule of the heavy oils might make two or more of the lighter ones.

4. **Derivatives of Methane.**—A derivative as the term is used here is a compound obtained by substituting an atom or atoms of some element or some radical group for one or more of the hydrogen atoms in the compound. One of the most simple as well as familiar derivatives of methane is chloroform, $CHCl_3$, obtained indirectly by substituting three atoms of chlorine for three of the hydrogen in methane. Iodoform, mentioned elsewhere, is a corresponding derivative with the formula, $CHI_3$. Carbon tetrachloride, mentioned as a good fire extinguisher, is also a derivative in which all the hydrogen in methane has been replaced by chlorine. Chloroform is a colorless, oily liquid of rather pleasant odor and not inflammable. Its use as an anesthetic is familiar. It has the advantage over ether that it may be used near an open flame without danger.

5. **The Alcohols.**—There are two, familiar to all, methyl, or wood alcohol, and ethyl or grain alcohol. They are derivatives of the first two paraffins: thus, $CH_4 \rightarrow CH_3OH$, and $C_2H_6 \rightarrow C_2H_5OH$, in both of which a hydroxyl group has been substituted for a hydrogen atom. Each of the paraffins has a corresponding alcohol, the higher ones in the series being white crystalline solids. Wood alcohol is obtained by the destructive distillation of wood in making charcoal. It is a colorless liquid, if pure, has a somewhat unpleasant odor, is very poisonous, inflammable and an excellent solvent for many

things. Because of this last property it has many uses as in making shellac, and similar preparations. However, *denatured* alcohol, being much cheaper, is fast taking the place of the wood alcohol in many cases. It is grain alcohol, adulterated by the addition of about 10 per cent of methyl or wood alcohol or some other liquid to render it more or less disagreeable in odor, and unfit for medicines, extracts or as a beverage. Adulterated, as mentioned, it is often called *methylated spirits.* The United States government has specified at least eight formulas for denaturing alcohol to meet the various demands of manufacturers. It now has very extensive uses. It is one of the most commonly employed substances to prevent the freezing of the water in radiators of motor cars and trucks. Ethyl alcohol is made from grains. These are kept damp and warm for several days till sprouted. During this time a *ferment* called *diastase,* present in the seed and provided by nature to convert the insoluble starch present into soluble form, so that the embryo plant and rootlets can use it, has changed the starch into a form of sugar. At the proper stage, learned by experience, the grain is heated to stop the process; it is then ground, yeast is added and fermentation begins whereby the sugar into which the starch was converted changes into alcohol and carbon dioxide. Thus,

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

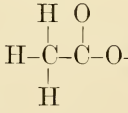
When the fermentation is completed the alcohol is distilled out and put upon the market about 95 per cent strength. If absolute alcohol is desired it may be obtained by treating the commercial variety with lime or anhydrous copper sulphate and distilling carefully. Grain alcohol is a colorless liquid, of pleasant odor, boil-

ing point of 78° C., and almost as poisonous as methyl. It is used in preparing many medicines as a solvent or preservative, in extracts for domestic or other purposes, and in a great variety of other ways.

6. **Organic Acids.**—From each of the alcohols, by oxidation, an acid may be derived. Thus, if two of the hydrogens in an alcohol are removed and an oxygen atom substituted for them, an acid is obtained. Methyl alcohol thus gives formic acid, HCOOH. The equations for the first two are

$$CH_3OH + O_2 \rightarrow HCOOH + H_2O,$$
$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O.$$

Like the paraffins and the alcohols, the acids differ by $CH_2$, so that the entire series is easily written. These two acids might be given thus, $H_2CO_2$ and $H_4C_2O_2$; but they are usually presented, as above, to indicate the structure of the molecule, and this is decidedly preferable. The empirical formula, $H_4C_2O_2$, tells nothing but the number of atomic weights of each element present, from which may be calculated the percentage composition: the graphic formula indicates that three hydrogen atoms are attached to one carbon atom, and that the two oxygen atoms are attached to the other carbon but not in the same manner, and that the remaining hydrogen atom is attached to the second oxygen. It is more fully shown thus,



The first acid has little commercial value. It is secreted by some ants and received its name from the Latin word

for ant, *forma*. It is also secreted by the stinger gland of such insects as the wasp, bee, and the hornet, when excited. The pure acid is a colorless liquid, and upon the skin causes intense pain and produces blisters. It is this acid injected hypodermically, that causes the pain when stung by any of the above insects. Acetic acid is widely used in a diluted form, 2 to 5 per cent, as vinegar. Originally, it was obtained largely from apple cider through, first alcoholic fermentation, when the cider became *hard*, and then subsequent oxidation by means of another species of bacterium. At the present time the demands are too great to be met in this way. Some is obtained in the distillation of wood in making charcoal; some in the fermentation of fruit juices other than that of the apple; but most comes from the glucose prepared from corn starch. A solution of the glucose is passed slowly through tanks or barrels filled with shavings, previously inoculated with the bacterium, *Mycoderma aceti*, familiarly known as "mother of vinegar." The process is rapid and the vinegar obtained is free from the many organic impurities of the old-time product, especially the decayed pulp of the apple. It also does not contain the vinegar eel, a tiny white worm, which frequently may be seen in countless numbers in cider vinegar if examined carefully. Pure acetic acid is a colorless liquid, which becomes solid at 16.7° C. It is often called *glacial acetic* for this reason.

7. **Aldehydes.**—From each alcohol in the series a corresponding aldehyde may be obtained. This is done by carrying the oxidation only far enough to remove two atoms of hydrogen without introducing anything in their place. This leaves them unsaturated compounds; hence, they are reducing agents. The only one of importance is *formaldehyde*, which is prepared from methyl

alcohol. All the aldehydes obtain their names from the corresponding acid, hence, the name in this case. The preparation from methyl alcohol is shown by the equation,

$$2CH_3OH + O_2 \rightarrow 2HCOH + 2H_2O.$$

Formic aldehyde is a gas which liquefies at −21° C. For use it is dissolved in water and is put on the market under the name of *formalin*, a 40 per cent solution. From this the gas is constantly escaping, irritating in odor, affecting both the nostrils and eyes. It is strongly germicidal and is used extensively for disinfecting purposes. This is easily done by pouring the solution upon lime with which the water present reacts giving sufficient heat to expel the gas rapidly. Since it is a hardener of tissues and cheaper than alcohol it is used extensively in preserving various zoological and botanical specimens.

8. **The Ethers.**—Corresponding to each alcohol is an ether. From ethyl alcohol is obtained the only important one, ethyl ether. Its formula is $(C_2H_5)_2O$, which indicates that it is an oxide of the ethyl group. It is a colorless liquid, of sweet pleasant odor, with a boiling point below the temperature of the human body, 34.9° C. It is very inflammable, and an excellent solvent of iodine, as also of oils and fats. Inhaled it produces anesthesia. It is regarded as a safer anesthetic than chloroform, but cannot be used near an open flame.

### Exercises for Review

1. What is a hydrocarbon? Name six with formulas. What is an organic compound? What is a paraffin?

2. How many paraffins are known? What is their physical condition?

3. Give two other names for methane. How does it receive these?

4. Describe the safety lamp and explain how it works.

5. Of what does gasoline consist? Into what several oils may it be separated? What is this process called?

6. Name two halogen derivatives of methane and use of each.

7. Name two alcohols with formulas. To what class of compounds do they belong?

8. What is denatured alcohol? Give some uses for it.

9. What is methylated spirits? What is a ferment?

10. How is grain alcohol made? Give uses.

11. Name two important organic acids. From what are they derived?

12. Where does each of these occur in Nature?

13. How is the commercial supply of vinegar obtained?

14. What is the common aldehyde? Its trade name? Uses for it?

15. Give formula for common ether. Of what use is it? Compare with chloroform.

## CHAPTER XVIII

## ETHEREAL SALTS, OILS, FATS, SUGARS

**Outline—**

Esters or Ethereal Salts
Glycerol
Esters of Glycerine
Oleomargarine
Compound Lards
Molecular Structure of Fats
The Olefins
Hydrogenation of Oils
The Carbohydrates
- (*a*) Monosaccharides
- (*b*) Disaccharides
- (*c*) Polysaccharides

1. **Esters.**—It will be remembered that a base is a hydroxide. By examining the formulas of the alcohols it will be seen that they are hydroxides. They are organic bases and, combined with organic acids, they produce what are called *ethereal salts* or *esters.* The first term is used for the reason that many of them have pleasant odors somewhat resembling ether. The word, *ester,* is coined from the other two and has no meaning. Several of these ethereal salts are familiar in the form of artificial flavors and extracts, such as banana, pineapple, and the like. They may be had of the grocers and are found at soda fountains in some of the syrups used. Thus, artificial pineapple is ethyl butyrate, an ester of grain alcohol and butyric acid. It is the latter that gives the strong, disagreeable taste to rancid butter; apple is amyl valerate, and pear, isoamyl acetate. The ester formed by the union of ethyl alcohol and acetic acid has a pleasant

fruity odor and is easily made in the laboratory. It is sometimes used as a test for the presence of alcohol in a substance.

2. **Glycerol.**—This compound is commonly known as glycerine. Its formula, $C_3H_5(OH)_3$, shows that it is an organic base with three hydroxyl groups; it is, therefore, an alcohol. It is obtained as a by-product of the soap industry. In home-made soaps it is not separated out and in some special varieties of factory-made, such as the transparent soaps. But the great demand for glycerine in the manufacture of explosives as described elsewhere and the fact that it adds little to the value of the soap for general purposes, has led to its careful separation. Glycerine is a sweet syrupy liquid, nearly colorless if pure and very soluble in water. It derives its name from the Greek word for *sweet* on account of its taste. Because of the fact that it is hygroscopic, when the price will permit, it is sometimes used in small quantities by bakers in cakes to prevent their drying out so rapidly. It is also used in toilet and other pharmaceutical preparations, but the greater proportion goes to the explosive factories.

3. **Esters of Glycerine.**—It is the salts of glycerine that chiefly interest us, for they are the common fats and oils used as foods. The four most common are

Glyceryl butyrate, Butyrin, $C_3H_5(C_3H_7COO)_3$,
Glyceryl palmitate, Palmitin, $C_3H_5(C_{15}H_{31}COO)_3$,
Glyceryl oleate, Olein, $C_3H_5(C_{17}H_{33}COO)_3$,
Glyceryl stearate, Stearin, $C_3H_5(C_{17}H_{35}COO)_3$.

All the common fats and oils are mixtures of three or all four of these. Butter contains all four; when free from water the butyrin is about 8 per cent of the whole. It is this ester that gives the characteristic pleasant odor

and taste to butter. Ordinarily, there is in butter about 12 to 14 per cent of water, with some casein from the milk. Olive oil is about 75 per cent olein. Of the four fats mentioned, olein has the lowest melting point, being a liquid at ordinary temperatures, and stearin has the highest. Any fat, therefore, with a high proportion of olein will melt easily and may be liquid at all ordinary temperatures; thus, cotton-seed oil and "mazola," an oil made from corn as a by-product in the manufacture of starch and glucose, are high in olein. Common lard is about 60 per cent olein and melts easily, while beef fat is high in stearin. It will be seen, therefore, that the various edible fats, whether from beef, pork, mutton, or of vegetable origin, are very similar in character. If the formulas given above are examined, this fact is even greatly emphasized.

4. **Oleomargarine.**—The demand for butter is far greater than the supply. This has led to the preparation of artificial butters, most of which are called oleomargarines. These are made by the mixture of animal and vegetable oils, which are much cheaper than butter. One formula, used by one of the large packing houses, is given below,

Neutral lard, 75 pounds
Cottonseed oil, 175 pounds
Oleo oil, 675 pounds
Peanut oil, 75 pounds

These are put into 60 gallons of milk from which the cream has been separated and churned. The purpose of this is to add something of the flavor of real butter and possibly some of the casein of the milk. The fats are removed from the milk, and 150 pounds of real butter and 125 pounds of salt are added and the whole

thoroughly worked together. This gives a total weight of solids of 1,275 pounds. In the churning and subsequent working of the mixture considerable water, even as much as 12 per cent is taken up, so that there is finally a total weight of between 1,400 and 1,500 pounds. In this variety it will be seen the butter is approximately 10 per cent of the whole. In another formula used, the real butter mixed with the other fats may run as high as 25 per cent, but it is understood that this particular brand is not put on the general market but sold entirely to special customers. Many brands contain no butter at all. At the present time oleos in which cocoanut oil enters to a very considerable extent are being manufactured by nearly all the large packing companies. The advantage claimed for these butters is that cocoanut oil contains about 5 per cent of butyrin; hence, they much more nearly approach real butter in composition and taste than do those with a higher percentage of animal oils. For years after their introduction into the United States there was great objection made to them by the butter producers and much adverse legislation resulted. They may not be colored, although all creamery butter and cheese are; moreover, oleos, must pay an excise tax, which somewhat increases their cost to the general public. Nevertheless, these artificial butters are clean, wholesome articles of food, nutritious, and to all purposes, of practically the same food value as the real article. There is only one objection and that is the low melting point; thus in warm weather oleomargarine is more difficult to keep as hard as is desirable. In spite of adverse legislation and the prejudice existing, their consumption has increased wonderfully in the last five years. Some idea of this may be obtained from the government reports concerning the importa-

tion of cocoanut and other vegetable oils. The following table gives the amounts for the years 1914 and 1918, the last available at this time.

| Oil | 1914 | 1918 |
|---|---|---|
| Peanut Oil | 1,000,000 gals. | Over 8,000,000 gals. |
| Soy Bean Oil | 16,000,000 lbs. | 337,000,000 lbs. |
| Cocoanut Oil | 74,000,000 " | 259,000,000 " |

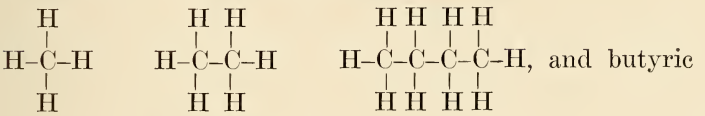
5. **Artificial Lards.**—As the high price of butter and the inadequate supplies have led to the substitution of oleos, so has it been in the case of lard. The demand is vastly greater than the supply and today a considerable number of so-called "compound lards" are found on the market. Such are "Suetene," "Cottolene," "White Cloud," "Snowdrift," and numbers of others. As the names of some indicate, many of them contain more or less of cotton-seed oil. But as this runs high in olein it is liquid at ordinary temperatures. The public is accustomed, however, to a *solid* fat for *shortening* and for various other food purposes; hence, it is slow to accept a liquid, however equally good it might be. Efforts were made, therefore, to overcome this difficulty, and these have been eminently successful as will be shown later in this chapter.

6. **Structural Composition of Fats.**—With the exception of olein the fats mentioned in this chapter may be regarded as derivatives of the paraffins. Thus, butane, $C_4H_{10}$, is the fourth in the paraffin series. The acid derived from it, butyric, would have the formula, $C_3H_7COOH$. Combining this acid with the base, glycerol, as shown by the equation,

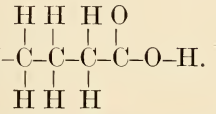
$$C_3H_5(HO)_3 + 3C_3H_7COOH \rightarrow 3H_2O + C_3H_5(C_3H_7COO)_3$$

we have butyrin. As the paraffins are all saturated compounds, so are the glyceryl salts derived from them. To

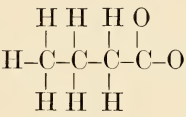
illustrate: Methane, ethane and butane are respectively represented by the structural formulas,



and butyric acid by



In all these it is seen that every carbon atom is fully saturated; so are the esters as may be seen in the following formula for butyrin. To the glyceryl radical, ($C_3H_5$) three carbon chains are attached, but only one is written for the sake of convenience,



7. **The Olefins.**—There is another class of hydrocarbons to which attention must be directed in order that the preparation of compound lards may be understood. These are the olefins, many in number, of which the first few of the series are given.

Ethylene, $C_2H_4$,
Propylene, $C_3H_6$,
Butylene, $C_4H_8$,
Amylene, $C_5H_{10}$, also called Pentylene,
Hexylene, $C_6H_{12}$.

It will be observed that they are given names derived from those of the paraffins, with the ending changed. There is no olefin corresponding to methane. These compounds may also form acids and alcohols as in the case

of the paraffins. The important distinction to be noticed at this time is that these are unsaturated compounds. A proof of this was given in the case of ethylene on p.

180. Structurally, this would be represented thus, $-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-$,

which shows two of the carbon atoms with one free *bond*. In the same way the acids and the esters derived from them would be unsaturated. Therefore, olein, belonging in this group, is an unsaturated compound. If the formulas for stearin and olein be compared, it will be observed that they differ only by two atoms of hydrogen, yet one is a hard white solid, and the other a liquid at ordinary temperatures. Without attempting to write the entire carbon chain, they may be compared thus,

$$\text{Chain of Carbon-}\overset{H}{\overset{|}{C}}\text{-}\overset{H}{\overset{|}{C}}\text{-}\overset{H}{\overset{|}{C}}\text{-}\overset{O}{\overset{||}{C}}\text{-O-}(C_3H_5) = 2 \text{ Carbon Chains,}$$

$$\text{Chain of Carbon-}\overset{H}{\overset{|}{C}}\text{-}\overset{H}{\overset{|}{C}}\text{-}\overset{H}{\overset{|}{C}}\text{-}\overset{O}{\overset{||}{C}}\text{-O-}(C_3H_5) = 2 \text{ Carbon Chains.}$$

The first of these is stearin, the second, olein.

8. **Hydrogenation of Oils.**—If the above statements are true it would seem that if it were possible to cause the unsaturated carbon atom in olein to take up two additional atoms of hydrogen, the olein should be changed into stearin with a corresponding change in melting point. This has been found possible and the process is called *hydrogenation*. A current of hydrogen introduced into any of these oils has no effect, but if a

catalytic agent be used, more often nickel in this case, the unsaturated olein takes up the additional hydrogen and at room temperature becomes a white solid. The process has the greatest commercial value. "Crisco," as well as the various compound lards mentioned, are vegetable oils, thus hydrogenated, or they are mixtures of the same with animal fats. Wesson oil is cotton-seed oil prepared by a certain process for cooking purposes. All the edible vegetable oils such as those made from corn, peanuts, cotton seed, soy beans, cocoanuts, are now being hydrogenated and made into pure white solid fats. They are all wholesome, probably even more so than those of animal origin, because not subject to disease and equally valuable as energy and heat producers.

9. **The Carbohydrates.**—The organic compounds considered thus far in this chapter have all been hydrocarbons and derivatives from them. There is another very important class known as the *carbohydrates,* which as the name indicates contain carbon, hydrogen and oxygen. The hydrogen and oxygen with scarcely any exception are in the proportion of 2 to 1. Three of the most common, which are typical of the three classes are

Glucose, $C_6H_{12}O_6$, a monosaccharide,
Cane Sugar, $C_{12}H_{22}O_{11}$, a disaccharide,
Starch, $(C_6H_{10}O_5)n$, a polysaccharide.

The prefixes *mono-*, *di-* and *poly-* refer to the number of aldehyde or ketone groups which the various compounds in these three classes contain. One aldehyde, HCOH, has been studied, but the ketones are not of sufficient importance to demand our attention here. The group -COH is contained in all aldehydes; glucose has one of these groups, cane sugar two, and starch several or many. Glucose is one of several sugars with the same empirical for-

mula, found in nature in various fruits. It is manufactured extensively from corn starch. The oil is first removed from the corn; in water under the action of dilute sulphuric acid, the starch takes up two additional atoms of hydrogen and one of oxygen for each saccharide group, thus,

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6.$$

The sulphuric acid used is merely catalytic and is removed by adding lime or some similar substance which converts it into an insoluble compound, so that it settles out. The glucose is then concentrated and put on the market mostly in the form of a syrup under a variety of trade names. One of the most advertised is "Karo," which may be had in a dark variety, the natural color, and a light variety, which has been bleached by sulphur dioxide. Glucose, while only about three-fifths as sweet as cane sugar, is a wholesome article of food notwithstanding a popular prejudice against it. This has come through a misunderstanding regarding the sulphuric acid used in the inversion of the starch. The bleached or colorless syrups may sometimes contain a trace of the gas used in the process of bleaching, but this objection cannot be offered to the dark syrups. Much of the candy on the market contains more or less glucose. Probably the only objection that can be offered is that it absorbs moisture from the air more readily than that made from cane sugar, and thus in damp weather tends to become "sticky." Glucose, as a food, is more readily assimilated than cane sugar; in fact, the latter, before assimilation, must be changed by the digestive fluids into the monosaccharide variety.

10. **The Disaccharides.**—Cane and beet sugar are the two most abundant of this class and have the same composition. Their source is well known and need not be

discussed here. Milk sugar, obtained as a by-product from the whey in cheese factories, differs from the two already mentioned in that it contains a molecule of combined water, thus, $C_{12}H_{22}O_{11}.H_2O$. Milk becomes sour through the changing of this sugar into lactic acid just as acetic acid is produced in cider through the fermentation of the fruit sugar contained in the apple. The lactic acid produced thus converts the casein, originally present in the soluble form, into the insoluble variety,

Fig. 46.—Starch granules. The shape of the granules is different in the various starch-containing foods, so that under the microscope the variety may be readily recognized.

so that the milk becomes "curdled." The same thing occurs in the stomach through the action upon the casein of the hydrochloric acid always normally present.

11. **Starches.**—A large number of plants produce starch. The most familiar to us are the grains, such as wheat and corn, and the potato. All have the same formula, but under the microscope, their granules are very different in shape (Fig. 46). The number of saccharide groups contained in the molecule is not known

as is indicated by the formula. Cellulose is represented by the same empirical formula, but probably the value of $n$ is different from what it is with the starches. It would seem possible, judging from the formulas of starch and cellulose, to convert such waste products as sawdust, which is largely cellulose, into a monosaccharide, as starch is made into glucose. No method, however, has ever been devised which is cheap enough, although experimentally it is entirely possible. When dry starch is heated to 250° C. it is converted into a product called dextrin; when made into a paste, it is used instead of mucilage extensively, especially upon envelopes, stamps, and for similar purposes. It is also employed largely in sizing paper, weighting cloth, paper for cardboard, and for sizing walls preparatory to papering. Paper is made from wood, straw, and various other articles which consist largely of cellulose. Another organic compound in the wood, known as liguin, is first removed by treatment with sodium hydroxide or some other chemical reagent, and the remaining cellulose washed thoroughly with water. The pulp is then rolled into sheets and dried. Filter paper is nearly pure cellulose.

### Exercises for Review

1. What is an ester? How did it receive the name? Name three.
2. What is glycerol? Formula? Where obtained?
3. Name four esters of glycerine.
4. Of what does butter consist? What is mazola?
5. What is oleomargarine? What advantages do the cocoanut oleos have?
6. What is a compound lard? Name some on the market.
7. Write the structural formula of butyric acid to show it is a saturated compound.
8. Name four olefins. How are they different from the paraffins?

9. How does olein differ from stearin?

10. What is meant by hydrogenation? What effect does it have on an oil? Can stearin be hydrogenated? Why?

11. What is a carbohydrate? Name three classes with example of each.

12. What is "karo"? How made?

13. Name three disaccharides. What is the origin of lactic acid in milk?

14. How is cellulose different from starch?

15. How is dextrin made? Uses?

16. Of what does paper consist mainly?

# CHAPTER XIX

## FOODS AND THEIR BODY VALUES

Outline—

- Classes of Foods
  - Carbohydrates
    - (*a*) Sugars
    - (*b*) Starches
    - (*c*) Cellulose
  - Oils and Fats
  - Proteins
  - Minerals

1. **Kinds of Foods.**—The various foods used may be classified as carbohydrates, oils and fats, and proteins, to which some add inorganic or mineral foods which may be made to include water.

2. **Carbohydrates.**—The carbohydrates most commonly used as foods are the various sugars, starch and cellulose. When sucrose, a general term for either cane or beet sugar, is boiled in the presence of an acid, it is slowly changed into glucose and fructose, both monosaccharides, called in this case, *invert* sugars. The process is called *inversion*. As the invert sugar obtained is not as sweet as the cane sugar used, in stewing any acid fruit for table use it is better not to add the sugar till the fruit is about done. By this plan less inversion takes place and less sugar is required to render the fruit palatable. Not only do acids have the catalytic action of inverting sugar, but certain enzymes as well. In our foods before sucrose is assimilated by the body it is converted into invert sugar by the enzymes of the digestive fluids. The sugars and starches serve mainly as

fuel and energy producers. Since they contain sufficient oxygen to convert the hydrogen present into water, it is the carbon content alone that determines the relative fuel value of a carbohydrate. In the body it combines with oxygen obtained through the lungs and heat results, just as if so much carbon in the form of coal were burned in a stove.

Starchy foods are obtained mainly from the various grains, wheat, corn, rice, rye, oats and barley; also from the potato, tapioca, arrowroot and sago. Bananas contain about 22 per cent of carbohydrates, much of which before the fruit is fully ripe is in the form of starch. When starchy foods are toasted, a portion of the starch is converted into dextrin, as is the outer portion of the crust of bread in baking. It is sweeter than starch, more soluble and more easily digested. All starchy foods, before digestion can take place, must be hydrolyzed or converted into invert sugar: this is partly accomplished in mastication through the action of the enzymes in the saliva. The equation shows the change, which is altogether catalytic,

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6.$$

Used in the body carbohydrates serve two purposes, giving energy for muscular exertion and warming of the body. When assimilated into the circulatory system they meet the oxygen and chemical union takes place, accompanied by heat. Any excess may be stored up in the muscles and liver in the form of an animal starch called *glycogen*. This may be used whenever an insufficient amount is furnished by the daily food.

Cellulose is found in many of our foods and is a carbohydrate as seen in the preceding chapter, but it is not an energy producer, for the reason that it is not

digestible. It is the enclosing wall of starch granules; it is abundant in the stems of plants. As maturity is reached in many vegetable foods, the quantity of cellulose increases. This is seen in asparagus, string beans, turnips, beets, celery and various others. It is what is spoken of as crude fiber in grains; the outside covering of wheat, corn, unpolished rice and other cereals. It is not capable of inversion by any of the enzymes of the body and for that reason, as stated above, is indigestible. Nevertheless, it plays a far more important part in digestion and the bodily health than most of us realize. It serves as a stimulant to the secretion of the fluids necessary for digestion and excretion and aids in increasing peristaltic action; in other words, it is a body-regulator food. Domestic animals such as the horse and cow use large amounts of what is called "roughness" or hay, much of which is cellulose. Fed on concentrated foods entirely they lose appetite and quickly become a prey for all sorts of diseases. In all probability a large proportion of the bodily ills of mankind may be traced directly to the use of foods too much refined and lacking in crude fiber or cellulose. Herein lies the health value of graham and bran breads and whole wheat foods and others of similar character.

**Pectin** is another vegetable carbohydrate found in the juices of many fruits and in the inner portion of the peeling of the orange and other citrus fruits. It is the principle involved in the making of jellies. It is coagulated by acids and also by sugar. In boiling fruit juice the water is removed and the pectin concentrated. The point is finally reached where coagulation takes place upon cooling. This is determined by the housewife by frequently testing small portions in a dish. For years numerous attempts were made to prepare

jellies from the cheaper grades of oranges regarded as unsalable by the packing houses, but all without success. Finally, it was found that in the orange the pectin is contained in the white portion of the peeling and not in the juice. Therefore when this portion is used with the juice of the fruit the operation is successful; and orange jelly and marmalade are now common articles of commerce.

3. **Oils and Fats.**—These foods are also heat and energy producing. One pound of this class is about the equivalent of 2¼ pounds of carbohydrates. This is because the amount of oxygen contained is much less in proportion in the fats and oils. They produce heat and energy in the same manner as the carbohydrates. In good assimilation any excess of such foods is stored up as glycogen in the liver, or as adipose tissue in various parts of the body, presumably to be used in cases of forced abstinence or as other needs might come.

4. **Protein Foods.**—Proteins are primarily muscle builders and not energy producing. It is true they may serve as body fuel, but as nitrogen is not oxidizable, they are poor in this respect and should never be used with this idea in view. The body contains about 18 per cent of proteins. Whenever work is done, or muscular exercise of any kind is taken, some of the cells of the tissues are torn down and must be replaced. Plants have the power of building their own protein from the carbon dioxide inhaled from the air together with the nitrogen and water absorbed from the soil. Some few, the legumes, through the aid of bacteria, may even obtain the needed nitrogen from the air. But no animal has such power. It must use, for replacing wasted muscular tissue, protein already formed; this may be either of animal or vegetable origin. Such foods as eggs, lean meat,

milk, cheese, beans, peas and other legumes are rich in protein. Several grains also furnish considerable protein if the whole of the grain is used. As protein serves mainly to restore wasted muscular tissue, the amount needed depends upon the amount of bodily exercise taken. In general, it may be said that not over 3 ounces, 80 grams, per day, are necessary, often much less. Those with sedentary employment require but little, while those engaged in manual labor need much. Too little regard is paid to this fact, with serious results to the bodily health. When carbohydrates are oxidized in the body, carbon dioxide and water are the sole products and these are eliminated largely through the lungs. Proteins, being nitrogenous foods, are converted into urea, $(NH_2)_2CO$, and this is eliminated through the perspiratory glands and by the kidneys. In case of ex-

TABLE OF FOOD VALUES OF CERTAIN NUTS

From Farmer's Bulletin, No. 332

| Nut | Waste % | Water | Protein | Fat | Carbohydrate | Fuel value per pound calories |
|---|---|---|---|---|---|---|
| Pecans | 50 | 3.4 | 12.1 | 70.7 | 12.2 | 3325 |
| Hickory | 62 | 3.7 | 15.4 | 67.4 | 11.4 | 3240 |
| Walnut | 59 | 3.4 | 18.2 | 60.7 | 16.0 | 3100 |
| Cocoanuts | 35 | 13.0 | 6.6 | 56.2 | 22.6 | 2825 |
| Peanuts | 27 | 7.4 | 29.8 | 43.5 | 17.1 | 2625 |
| Chocolate | — | 5.9 | 12.9 | 48.7 | 30.3 | 2770 |
| Cocoa | — | 4.6 | 21.6 | 28.9 | 37.7 | 2255 |

SOME DRIED FRUITS

| Fruit | Waste % | Water | Protein | Fat | Carbohydrate | Calories |
|---|---|---|---|---|---|---|
| Dates | 10 | 15.4 | 2.1 | 2.8 | 78.4 | 1575 |
| Raisins | 10 | 14.6 | 2.6 | 3.3 | 76.1 | 1560 |
| Figs | — | 18.8 | 4.3 | 0.3 | 74.2 | 1435 |
| Prunes | 15 | 22.3 | 2.1 | — | 73.3 | 1370 |
| Apples | — | 28.1 | 1.6 | 2.2 | 66.1 | 1320 |

## SOME FRESH FRUIT

| FRUIT | WASTE % | WATER | PROTEIN | FAT | CARBOHYDRATE | CALORIES |
|---|---|---|---|---|---|---|
| Banana | 35 | 75.3 | 1.3 | 0.6 | 22.0 | 450 |
| Grapes | 25 | 77.4 | 1.3 | 1.6 | 19.2 | 435 |
| Plums | 5 | 78.4 | 1.0 | — | 20.1 | 380 |
| Cherries | 5 | 80.9 | 1.0 | 0.8 | 16.7 | 355 |
| Pears | 10 | 84.4 | 0.6 | 0.5 | 14.1 | 285 |
| Apples | 25 | 84.6 | 0.4 | 0.5 | 14.2 | 285 |
| Orange | 27 | 86.9 | 0.8 | 0.2 | 11.6 | 235 |
| Peach | 18 | 89.4 | 0.7 | 0.1 | 9.4 | 185 |

## FOOD VALUES OF CEREAL PRODUCTS

| NAME | WATER % | PROTEIN | FAT | CARBOHYDRATE | CALORIES |
|---|---|---|---|---|---|
| Crackers | 5.9 | 9.8 | 9.1 | 73.1 | 1875 |
| Rolled Oats | 7.7 | 16.7 | 7.3 | 66.2 | 1800 |
| Shredded Wheat | 8.1 | 10.5 | 1.4 | 77.9 | 1660 |
| Graham Flour | 11.3 | 13.3 | 2.2 | 71.4 | 1630 |
| Macaroni | 10.3 | 13.4 | 0.9 | 74.1 | 1625 |
| Hominy | 11.8 | 8.3 | 0.6 | 79.0 | 1610 |
| White Flour | 12.8 | 10.8 | 1.1 | 74.8 | 1610 |
| Rice | 12.3 | 8.0 | 0.3 | 79.0 | 1590 |
| White Bread | 35.0 | 9.1 | 1.6 | 53.3 | 1200 |
| Graham Flour | 35.7 | 8.9 | 1.8 | 52.1 | 1180 |

## FOOD CONTENT OF CERTAIN VEGETABLES

| NAME | WATER % | PROTEIN | FAT | CARBOHYDRATE | CALORIES |
|---|---|---|---|---|---|
| Sweet Potato | 20 | 1.8 | 0.7 | 27.4 | 560 |
| Irish Potato | 20 | 2.2 | 0.1 | 18.4 | 380 |
| Parsnips | 20 | 1.6 | 0.5 | 13.5 | 295 |
| Onions | 10 | 1.6 | 0.3 | 9.9 | 220 |
| Beets | 20 | 1.6 | 0.1 | 9.7 | 210 |
| Carrots | 20 | 1.1 | 0.4 | 9.3 | 205 |
| Turnips | 30 | 1.3 | 0.2 | 8.1 | 180 |
| Cabbage | 15 | 1.6 | 0.3 | 5.6 | 145 |
| Cauliflower | — | 1.8 | 0.5 | 4.7 | 140 |
| Spinach | — | 2.1 | 0.3 | 3.2 | 110 |
| Celery | 20 | 1.1 | 0.1 | 3.3 | 85 |
| Cucumber | 15 | 0.8 | 0.2 | 3.1 | 80 |
| Green Peas | 45 | 7.0 | 0.5 | 16.9 | 455 |
| String Beans | 7 | 2.3 | 0.3 | 7.4 | 190 |
| Squash | 50 | 1.4 | 0.5 | 9.0 | 210 |
| Tomatoes | 10 | 0.9 | 0.4 | 3.9 | 105 |

cess, uric acid forms and tends to accumulate in the muscles and about the joints and causes rheumatism. Those in sedentary employments, therefore, should use little meat or other nitrogenous foods. Nitrogenous foods in decomposing often produce what are called *amines*. These are substitution products of ammonia, one of which is $NH_2CH_3$, methyl amine. Some of these are very poisonous and are called *ptomains*. In tables showing content of protein in various food products, the amount is often given in terms of nitrogen. As on an average the nitrogen in a protein is 16 per cent, to determine the amount of protein contained the nitrogen must be multiplied by 6.25. The preceding tables show the food content and the fuel or calorific value of a large number of common articles of diet:

5. **Mineral Foods.**—In all foods used there are small quantities of mineral matter or ash. These come from the soils and are taken up by the growing plant. While the amounts are small, certain portions seem necessary for health. The blood owes its color to the presence of iron compounds, and certain foods especially are relatively rich in these. Such are eggs, milk, peas, beans, figs, dates, raisins, wheat, rye, barley, and spinach. Calcium and phosphorus, usually combined as a phosphate, are especially needed in youth, but more or less at all times. The dry bone is over 50 per cent calcium phosphate, while other portions of the body also contain smaller amounts. This must, therefore, be supplied. Such foods as milk, eggs, cheese, whole wheat, nuts and beans are rich in phosphorus. White flours are made by milling off the outer portions of the grain; hence, the cellulose and the mineral portions are lost as foods with serious consequences to the bodily health. In the body are also found sodium, potassium, magne-

sium, chlorine and sulphur. More than sufficient sodium and chlorine are supplied in the common salt used. Sulphur is contained in such foods as eggs, and often in other protein foods. Magnesium and potassium are found in various nuts, cocoa, beans, peas, prunes,

*a* *b* *c* *d* *e* *f* *g* *h* *i* *j* *k* *l*

Fig. 47.—Foods rich in iron. (From Greer's Textbook of Cooking.) *a*, Peas; *b*, figs; *c*, wheat; *d*, lentils; *e*, spinach; *f*, dates; *g*, eggs; *h*, rye; *i*, beef; *j*, beans; *k*, raisins; *l*, lima beans.

figs, raisins, oats and rye. The following tables give the quantity of mineral matter contained in a number of common articles of diet. The value of water in the human economy has been discussed elsewhere.

FOODS RICH IN IRON

The following contain .003 per cent or more

| | | |
|---|---|---|
| Beans, dry | Lean beef | Whole barley |
| Dates | Peas, dry | Whole rye |
| Eggs | Raisins | Whole wheat |
| Figs, dried | Spinach | |

FOODS RICH IN PHOSPHORUS

The following contain .9 per cent or more

| | | |
|---|---|---|
| Beans, dry | Cocoa | Peas, dry |
| Cheese | Eggs, the yolk | Whole wheat |
| Chocolate | Peanuts | |

*a* *b* *c* *d* *e* *f* *g* *h*

Fig. 48.—Foods rich in phosphorus. (From Greer's Textbook of Cooking.) *a*, Peas; *b*, chocolate; *c*, beans; *d*, peanuts; *e*, whole wheat; *f*, cheese; *g*, cocoa; *h*, yolk of egg.

Figs. 47 and 48 show graphically what is given in the tables. (From Greer's Textbook of Cooking.)

### Exercises for Review

1. Name the four classes of foods.

2. What is meant by inversion? Why should the sugar be added after the fruit has about finished cooking?

3. Why is cellulose not digestible? Of what value is it to the body? What is meant by crude fiber?

4. What is pectin? Of what practical value is it in the household? Where is it found in most fruits? Any exception?

5. What is the use of carbohydrate foods in the body? Why is a fat of greater fuel value than a sugar?

6. Explain how the heat is produced in the body. How are the products of combustion in the body eliminated?

7. Of what do protein foods consist? Name some typical ones.

8. What value has a protein food to the body? How much of this kind of food is needed per day?

9. Into what is protein food converted when it has been used in the body? How is it removed?

10. In case of excess of protein foods what is apt to follow? How remove this condition?

11. Name the more common mineral foods. From what may the three most important be obtained?

12. What do most "tonics" contain? What is the supposed purpose?

# CHAPTER XX

## SOLUTION AND IONIZATION

**Outline—**

- Meaning and Kinds of Solution
- Concentration of Solutions
- Characteristics of Solutions
  - (*a*) Change in Freezing Point
  - (*b*) Rise in Boiling Point
  - (*c*) Difference in Density
- Law of Variation
- Noted Exceptions
- Cause of Variation
- Conductivity of Solutions
- Dissociation
  - (*a*) By Heat
  - (*b*) By Solution
- Ionization and Ions
- Ions and Valence
- Ions and Chemical Action

1. **Definition of Solution.**—As generally defined a solution is a homogeneous mixture of two or more substances. Usually we think of it as a solid in a liquid, for such are the more common. The *solvent* is the substance of greater amount, while the *solute* is the other. Thus, if a few grams of salt be dissolved in a liter of water, the salt is the solute and the water is the solvent. There are several kinds of solutions besides that of a solid in a liquid. For example, air is a solution, in which the nitrogen is the solvent. Soda water is a solution of a gas, carbon dioxide, in water; a silver dollar is a solution of 10 parts of copper in 90 of silver. However, as solutions of solids in liquids are by far the most common, it is with them that this chapter deals.

2. **Solution Concentration.**—The properties of solutions differ from those of the solvent. For the sake of comparisons it is necessary to agree upon some standard when speaking of the strength of a solution. If a gram molecular weight of any substance be dissolved in a liquid so as to make one liter of the mixture, the solution is said to have a *concentration of one*, and is marked $C_1$. If a liter of a solution contains 2 gram molecular weights of the solute, its concentration is *two*, marked $C_2$. Obviously, a gram molecular weight of sugar would contain the same number of molecules as a gram molecular weight of salt, although the former would contain 342 grams and the latter only 58.46 grams. So in all solutions with a concentration of one there would be the same number of molecules of the solute.

3. **Characteristics of Solutions.**—As there is always a diminution of volume when two substances are mixed homogeneously, the specific gravity of the solution is always greater than that of the solvent. Again, the freezing point is always lower than that of the solvent, and the boiling point is higher, or, as it is usually expressed, the *vapor pressure is lowered.* A little thought will make all three statements apparent. As a small handful of salt may be dissolved in a quart of water without greatly increasing the volume, evidently the water per cubic centimeter is heavier than before the salt was added. Heat is merely a form of molecular energy; when a body is warmed its molecules are made to move faster; when cooled their motion becomes slower. Therefore, since there are more molecules in a given volume of a solution than in the same volume of the solvent, it would take more heat energy to set them in motion or, on the other hand, to stop them than if dealing with the pure solvent. In other words, speaking of *cold* as if it were

a force, it would require a greater degree of cold to "slow down" the larger number of molecules in the solution than it would the fewer number in the solvent, that is it is harder to freeze salt water than pure. Likewise, in bringing a solution to the boiling point, there would be more molecules to which there must be imparted a certain velocity before boiling begins, so the temperature would be higher before the boiling is reached. From the fact that a liquid begins to boil when the *pressure* of the vapor passing off from it equals or is slightly in excess of the atmospheric pressure above it, we usually say the *vapor pressure* is lowered instead of saying the boiling point is raised, but both expressions mean the same thing.

4. **Concentration and Freezing Point Lowering.**— Since all solutions with a concentration of one contain the same number of molecules of the solute per liter, it would seem from the kinetic viewpoint that the freezing point of all solutions, no matter what the solute, would be lowered the same for the same solvent. That is, if pure water freezes at 0° C. and a solution containing a gram molecule of sugar per liter freezes at –1.8° C., we should expect a solution of alcohol containing a gram molecule per liter also to freeze at 1.8° below zero. Likewise we should expect such solutions with a concentration of two, that is with 2 gram molecules of the solute per liter, to freeze at –3.6°. If such experiments are made, using any of the soluble organic compounds mentioned in the preceding chapters, our expectations are realized. These facts, then, are stated in this conclusion, that the lowering of the freezing point of a solution is directly proportional to the concentration. Briefly it is expressed thus,

$$L \propto C,$$

in which L means lowering of freezing point and C the

concentration, and the sign, $\propto$, *varies as*. Experiments made upon the lowering of the vapor pressure of such solutions, show like results, so that the same formula may be applied to both cases. In tabular form below are shown some of the solutions commonly used with results upon the freezing point:

TABLE OF FREEZING POINT LOWERING

| SUBSTANCE | CONCENTRATION | FREEZING POINT | GRAMS PER LITER |
|---|---|---|---|
| Alcohol | C = 1 | −1.8 | 46 |
| Glucose | C = 1 | −1.8 | 186 |
| Cane Sugar | C = 1 | −1.8 | 342 |
| Glycerine | C = 1 | −1.8 | 92 |
| Alcohol | C = 2 | −3.6 | 92 |
| Glucose | C = 2 | −3.6 | 360 |
| Cane Sugar | C = 2 | −3.6 | 684 |
| Glycerine | C = 2 | −3.6 | 184 |
| Alcohol | C = 3 | −5.4 | 138 |

The results given above have disregarded slight variations due to experimental errors or otherwise easily accounted for; they show conclusively what was previously stated that the lowering of the freezing point depends upon the concentration.

5. **Exceptions to the Above.**—It will be noticed that all the substances given in the table are organic compounds. We should expect the same results, however, with the inorganic compounds, such as common salt, sulphuric acid, potassium chloride, and others familiar to us. When such are tried, using a concentration of one, the same as before, so as to introduce the same number of molecules per liter, the results do not agree at all. In some cases the freezing point is lowered nearly twice as much, in others nearly three times, and still others nearly four times as much as expected.

6. **Cause of This Irregularity.**—It has been observed that chemical reactions between substances perfectly dry are practically *nil*. Pure dry hydrogen chloride does not react with zinc. It has been said elsewhere, Chapter I, that compounds, inorganic, are composed of an electropositive and an electronegative portion and that each gives a separate test. In the absence of all water such tests cannot be made. With the organic compounds this is not true. They are not composed of a positive and a negative part and tests with them are tests upon the substance as a whole. It seems then that when an inorganic compound is dissolved in water, in some way the positive and negative portions are separated from each other so that each may be tested. Further, it was noticed that such compounds as common salt, potassium chloride, hydrochloric acid, ammonium chloride and many others, which were possible of separation into only two particles, *one* positive and *one* negative, always gave a lowering of freezing point almost double that of the organic compounds when concentration of one was used. Further, such compounds as calcium chloride, $CaCl_2$, barium chloride, $BaCl_2$, sulphuric acid, $H_2SO_4$, calcium hydroxide, $Ca(HO)_2$ and many others capable of breaking up into three portions, two positive and one negative or one positive and two negative, in concentrations of one gave a lowering of freezing point nearly three times what the organic compounds did with the same concentration. Again, aluminum chloride, $AlCl_3$, phosphoric acid, $H_3PO_4$, capable of breaking up into four parts, gave a lowering of the freezing point almost four times that given by the organic compounds in solutions of the same strength. From conclusions already reached in the case of the organic compounds,—namely, that the lowering is proportional to the concentration,

it came to be believed from the above observations that in water the inorganic compounds are broken up into *parts* and exist there not as molecules but as parts of molecules. If this be true, a solution of potassium chloride, for example, would have as many *particles* to be "slowed down" in their movement as if the concentration were two; that is, the freezing point should be lowered 3.6°. Likewise, such substances as sulphuric acid, or calcium chloride in solution would contain as many particles as of the organic compounds with a concentration of three, and should give a lowering of 5.4°.

7. **Variation from Regular Lowering.**—In all these cases, however, the lowering falls short of the theoretic amount, as shown by the following table:

LOWERING OF FREEZING POINTS

| Substance | Concentration | Degrees Lowered |
|---|---|---|
| Cane Sugar | 1 | 1.8 |
| Grain Alcohol | 1 | 1.8 |
| Sodium Chloride | 1 | 3.5 |
| Calcium Chloride | 1 | 5.1 |
| Aluminum Chloride | 1 | 6.8 |

Thus it will be seen that the greater the number of possible particles into which the compound may be broken the greater the variation from the theoretic value. According to the kinetic theory, not only are the molecules of a body in motion, but the atoms likewise in the molecule. Some years ago it was shown by the great Dutch chemist, van't Hoff that in dilute solutions the molecules of the solute are at such distances from each other that they obey all the gas laws. In these cases, therefore, the parts into which the molecules are broken would be moving in all directions, and in all probability

would collide more or less frequently. For example, if potassium chloride is broken up into potassium and chlorine particles, in their movement the potassium and chlorine would more or less frequently collide and thus a molecule of the salt would be reformed. Among billions of particles with a rapid motion these collisions would be frequent, so that there would always be, except in cases of very great dilution, a very appreciable number of the molecules not broken up. Therefore, the number of particles in the solution, to be "slowed down," would never be quite double the number of the molecules, and, hence, the freezing point would not be lowered fully twice as much as in the case of the organic compounds. The same way with the calcium chloride, aluminum chloride and others: there being more particles per degree of concentration, since each molecule may break up into three or four parts, collisions would be more frequent, more molecules would exist intact, and the lowering would vary further from three or four times the theoretic amount.

8. **Conductivity.**—It was long ago observed that such substances as sugar, and the organic bodies are not conductors of electricity, either by themselves or dissolved in water. It has also been seen that pure water is not a conductor. Inorganic compounds, which have been found to give very irregular results in lowering of freezing point, are not conductors when in the solid form, but dissolved in water are almost universally good conductors. Such substances are spoken of as *electrolytes*, while those which will not conduct a current when dissolved in water are called *nonelectrolytes*. From the above observations and further, that when solutions of the inorganic compounds are electrolyzed the metal always appears at the cathode and the nonmetal at the anode, it

was thought possible that the positive particles might be the means of conducting the current through the solution and of giving it up to the negative electrode. Furthermore it was concluded that organic compounds are not conductors, because in water they are not broken up into particles so as to make it possible for one portion to be attracted toward the negative electrode.

9. **Dissociation.**—It has been seen in a very considerable number of cases that at different temperatures substances may exist with molecules of differing composition. Thus, nitrogen peroxide, at a temperature of about 23° C., has a molecular weight of 92, while at about 135° it is only 46, and at temperatures between these two it varies, being lower as the temperature is raised. As the molecular weight of 92 would correspond to the formula, $N_2O_4$, and 46 to that of $NO_2$, there can be only one explanation and that is that heat decomposes nitrogen tetroxide, and at a certain point this decomposition is complete, whereas at temperatures lower than this there are always present molecules of the greater density mixed with the lighter ones. This is shown by the equation,

$$N_2O_4 \rightleftarrows 2NO_2,$$

which means that the process is reversible and, what is more, is probably occurring at all times. When the temperature is lowered the reverse action is more rapid than the direct till a certain definite proportion is reached when equilibrium obtains. Such a reaction as this is called *dissociation*. Defined, dissociation is the decomposition of a substance and the reforming of the same by the union of the products, when the decomposing cause is removed. Likewise, ammonium chloride, heated, decomposes into ammonia and hydrogen chloride, but when the

two gases are carried away from the source of heat they recombine to form ammonium chloride. Thus,

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

Again, iodine vapor, below 700° C. shows a density of about 127 compared to hydrogen or a molecular weight of 254, which indicates $I_2$ for the formula. Above 700° C. the density rapidly decreases and at about 1,700 it is only half what it was at 700. The same thing has occurred as in the case of the nitrogen peroxide and may be represented thus,

$$I_2 \rightleftarrows 2I.$$

Many others might be given. Such cases are spoken of as *dissociation by heat.*

10. **Dissociation by Solution.**—As heat may be the means of dissociating substances, so it is believed liquids may be. When this occurs it is called *dissociation by solution*, or *ionization.* Because of the fact that dissociation by solution permits of conductivity and the electrolysis of the substance dissolved, it is often called *electrolytic dissociation,* but it must be remembered that electricity has nothing to do with the dissociation. Further, since in dissociation by this means the particles formed are able to be attracted to the electrodes of an electric circuit, they are believed to be electrically charged; hence, an equation representing the results of the dissociation of potassium chloride in water would be thus,

$$KCl \rightleftarrows \overset{+}{K} + \overset{-}{Cl},$$

and of zinc sulphate,

$$ZnSO_4 \rightleftarrows \overset{++}{Zn} + \overset{--}{SO_4}.$$

These electrically charged particles, whether atoms or groups of atoms, are called *ions*, from a Greek word

meaning *to travel.* They were so named because of the fact of their constant movement from place to place. Ionization would be, therefore, the dissociation of a substance into ions.

11. **Kind of Ions.**—Ions are either *positive* or *negative* according to whether they are attracted to the cathode or the anode in an electrolyte. As already indicated, hydrogen, ammonium and the metals may form positive ions, called *cations* or *cathions,* because they are attracted by the cathode: the nonmetals, hydroxyl, and many oxygen radicals, like $-SO_4$, form negative ions, called *anions,* attracted to the anode. Ions are also spoken of as *simple*

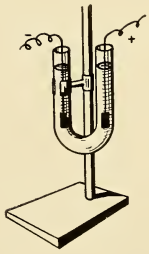


Fig. 49.—Ionization of a solution of common salt, and proof of same.

and *complex.* A simple ion consists of a single atom, electrically charged, while a complex ion contains more than one atom, that is an electrically charged radical, like –HO. It must be remembered that ions are not atoms. A solution of potassium chloride abounds in chlorine ions, but it possesses none of the properties of free chlorine—no color, no odor, no bleaching properties. The electric charge upon it, like an efficient rain coat not only prevents its "solution" in water, as it were, but also from doing the other things free chlorine would do. A very simple experiment shows the movement of the ions toward the electrodes in a solution. If salt water, colored with

litmus cubes, be put into the U-tube, as shown in Fig. 49, and the terminals of a battery be inserted, in a very short time the blue color at the anode will disappear. The chlorine ions have been attracted to this arm, and, coming in contact with the positively charged carbon or platinum electrode, have lost the charge they held by having it neutralized. Now, they have become *atoms* of free chlorine. Immediately, they begin to bleach the litmus solution and decompose the water. Likewise, the odor of free chlorine becomes apparent as well as the color, if the process is continued long. If the salt water had been colored by a red litmus solution the anode arm would have been bleached as before while at the cathode the solution would have turned blue. The sodium ions move toward the cathode; on meeting it they give up their positive charge to the electrode, become *atoms* of sodium, and immediately begin to decompose the water there. Thus,

$$2Na + H_2O \rightarrow H_2 + 2NaHO.$$

The hydrogen escapes in bubbles as can easily be seen, and the hydroxyl ions of the sodium hydroxide change the red litmus to blue. This, as has been stated elsewhere, is characteristic of all soluble hydroxides. Phenolphthalein is a coal tar product, which by soluble hydroxides is turned a beautiful violet-red color. In the above experiment, if a few drops of an alcoholic solution of phenolphthalein be added to the salt solution instead of coloring with litmus, the solution at the cathode quickly turns pink, when the current is passed, showing the formation of a hydroxide just as before.

12. **Ions and Valence.**—It will be noticed that the hydrogen ion was written above $\overset{+}{H}$ while that of zinc was $\overset{++}{Zn}$. It will be found that the electric charge

upon an ion is the same as the valence. In making hydrogen, experimentally, it was found that one atomic weight of sodium displaces one atomic weight of hydrogen from water and that one of zinc displaces two of hydrogen from acids. From this it would be seen that the valence of sodium is one and that of zinc is two. The ions, therefore, would carry single and double charges, respectively, $\overset{+}{\mathrm{Na}}$, $\overset{++}{\mathrm{Zn}}$.

13. **Chemical Action Ionic.**—It has been seen that a piece of zinc dropped into pure dry hydrogen chloride liquefied, shows no chemical action, but if water be added it becomes vigorous immediately. Likewise, zinc in concentrated sulphuric acid in making hydrogen gives very indifferent results. Ferrous sulphide in concentrated sulphuric acid shows almost no chemical action at all. In both of the last cases the addition of water brings vigorous results. It is believed from these and a very large number of other experiments, all indicating the same thing, that chemical action takes place between ions. In terms of the kinetic theory the presence of the water results in the ionization of the compounds, and the ions, moving through the solution in all directions, meet each other and form new combinations. Thus,

$$\mathrm{KCl} \rightleftarrows \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Cl}},$$

$$\mathrm{AgNO_3} \rightleftarrows \overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}}.$$

If these two solutions are poured together collisions between the potassium and silver ions are impossible, because being with like charge, as they approached each other repulsion would take place; likewise, the chloride ion and nitrate ion. But collisions between potassium ions and nitrate ions, also between chloride and silver ions could occur and would, as well as those indicated

by the equations. But silver chloride is an insoluble compound, and hence could not ionize; therefore, as fast as silver chloride formed it would separate out from the solution. Ultimately, all the silver and chloride ions would have collided and been removed, at which time there would be solid silver chloride which would be in the form of a precipitate, potassium ions and nitrate ions, with some molecular potassium nitrate.

14. **Other Types of Reactions.**—In the case just given one of the products is in the form of a precipitate and is thus removed from the sphere of action. The same is true if one of the products is a gas. Thus, if lime water is added to a solution of ammonium chloride, these steps would result,

$$NH_4Cl \rightleftarrows \overset{+}{N}H_4 + \overset{-}{C}l,$$
$$Ca(HO)_2 \rightleftarrows \overset{++}{C}a + \overset{-}{H}O + \overset{-}{H}O,$$
$$\overset{+}{N}H_4 + \overset{-}{H}O \rightleftarrows NH_4HO,$$
$$\overset{++}{C}a + \overset{-}{C}l + \overset{-}{C}l \rightleftarrows CaCl_2.$$

Now if the solution is warmed as is done in preparing ammonia, the following results,

$$NH_4HO \rightarrow NH_3 + H_2O.$$

Ammonia, being a gas, is constantly escaping, so that the ammonium hydroxide is being removed all the time. Therefore, the ammonium ions are being removed and the final result is calcium chloride in water ionized as shown by the equation,

$$\overset{++}{C}a + \overset{-}{C}l + \overset{-}{C}l \rightleftarrows CaCl_2.$$

This is typical of all cases in which one product is a gas. There are many others in which all the products are

soluble in water. Thus, when potassium nitrate and sodium chloride are mixed in solution,

$$KNO_3 \rightleftarrows \overset{+}{K} + \overset{-}{NO_3},$$
$$NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl}.$$

Very shortly there would be some potassium chloride molecules and some sodium nitrate molecules from the inevitable collisions; but these products are both soluble in water and would both ionize, thus,

$$KCl \rightleftarrows \overset{+}{K} + \overset{-}{Cl},$$
$$NaNO_3 \rightleftarrows \overset{+}{Na} + \overset{-}{NO_3}.$$

Evidently nothing is removed from the sphere of action in this case, and when equilibrium is reached, there are small amounts of all four compounds as well as large numbers of all four ions shown. Such chemical actions do not go to *completion* as is the case when one product is either a gas or a precipitate.

15. **Strong Bases and Strong Acids.**—Frequent use is made of the terms *strong* and *weak* acids and bases, and a clear understanding must be had. A strong acid or base is one that is largely ionized in solution. Since chemical action is between ions, where few ions exist there can be little action. Sulphuric and hydrochloric are spoken of as strong acids; this simply means that in aqueous solutions they dissociate so as to produce a large number of hydrogen ions. On the other hand, such acids as carbonic and acetic are regarded as weak acids for the reason that in solution they are not ionized greatly. In concentrations of one, strong acids will be ionized fully 75 per cent, while weak acids not over one molecule in something over 50,000 is dissociated. The same is true of bases. Sodium hydroxide dissolved in water is largely

broken into ions so that the quantity of hydroxide ion is large; on the other hand, copper hydroxide is a weak base because of the portion which dissolves only comparatively few of the molecules are ionized.

### Exercises for Review

1. Define the terms solution, solvent, solute.

2. Name seven kinds of solutions and give an example of each. What is the most common kind?

3. What is meant by a concentration of one in a solution? Give examples.

4. What is meant by a gram molecular weight of a substance?

5. Name three respects in which a solution differs from the solvent.

6. Explain why the specific gravity of a solution is greater than that of the solvent.

7. Explain by the kinetic theory why a solution has a lower freezing point than the solvent. Why should the boiling point be raised?

8. What is meant by the expression, vapor pressure is lowered?

9. What relation is there between lowering of freezing point and concentration of the solution?

10. If 1 c.c. of a solution of sugar of concentration one contains a thousand molecules, how many would a solution of glucose contain if the concentration were the same?

11. What kind of substances affect freezing point irregularly? Why is this?

12. With a concentration of one, how much would a solution of potassium chloride lower the freezing point? $CuSO_4$? $BaCl_2$? $PtCl_4$?

13. To prove that a solution contained silver nitrate, how many tests would have to be made? For what?

14. To prove that a solution contained alcohol, how many tests would be made? For what?

15. Why does a solution of calcium chloride, $CaCl_2$, not lower the freezing point three times 1.8, if it is capable of being broken into three particles?

16. What is an electrolyte? Name five. Name five nonelectrolytes.

17. Why are electrolytes conductors?

18. What is meant by dissociation? Illustrate.

19. Name two kinds of dissociation. What is ionization?

20. Define ion. Name four kinds with examples of each.

21. How is an ion different from an atom? Illustrate with the chloride ion.

22. Give some experiment to show that ions are free to move.

23. If alcohol were put into a U-shaped tube and the terminals of a battery inserted, what would collect at the anode? Cathode?

24. What relation is there between ionic charges and valence? Illustrate.

25. When chemical change takes place in a solution between two substances, explain what really happens.

26. Why does concentrated sulphuric acid not react with ferrous sulphide?

27. Write the ions formed by sulphuric acid in water; also ferrous sulphide, FeS. Show by ionic equations what happens when they are put together.

28. Write the ionic equations showing what happens when potassium bromide and silver nitrate are put together in a solution.

29. What is meant by a reaction going to completion? Give two classes of reactions in which this happens.

30. Knowing that barium sulphate is not soluble in water, when sodium sulphate, $Na_2SO_4$, and barium chloride, $BaCl_2$, are put together, write the ionic equations and state whether the reaction would go to completion.

31. What is meant by a strong acid? A strong base? Illustrate.

# CHAPTER XXI

## SULPHUR AND COMPOUNDS

**Outline—**

- Occurrence of Sulphur
- Method of Preparation
- Characteristics
  - (*a*) Physical
  - (*b*) Chemical
- Uses
- Compounds
  - Hydrogen Sulphide
  - The Oxides
  - Sulphurous Acid
  - Sulphuric Acid
    - (*a*) Chamber Process
    - (*b*) Contact Process
    - (*c*) Characteristics and Uses
  - Thiosulphuric Acid
  - Sodium Thiosulphate

1. **Occurrence in Nature.**—Sulphur has been known from remote times. It is found free in abundant quantities in volcanic regions such as those of Sicily. Near the western entrance to Yellowstone Park vast quantities in a free but impure form occur in what are known as the Sulphur Mountains. In Louisiana, at a distance of several hundred feet below the surface, are vast amounts of nearly pure sulphur, deposited in earlier ages probably through bacterial action upon sulphur compounds. Gypsum, calcium sulphate, as well as a large variety of other sulphur compounds, occur widely distributed, some of which may be used as a source of sulphur.

2. **Method of Preparation.**—At the present time Louisiana furnishes by far the greater part of the sulphur needed by the United States. The process is very similar to that used for obtaining salt from underground deposits. Fig. 50 will make the plan clear. By drilling, a hole 6 or 8 inches in diameter is sunk until it reaches the sulphur deposit. Four concentric pipes are then inserted; through the two largest, water heated under pressure to a temperature of about 170° C. is run down upon the sulphur bed. Upon the innermost

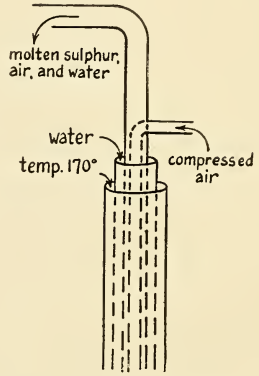



Fig. 50.—Method of obtaining sulphur in Louisiana.

pipe pressure is secured by compressed air: in this way molten sulphur, hot water and air flow out through the remaining pipe into large bins. Here the sulphur solidifies while the water is conducted away. The sulphur thus obtained is sufficiently pure for all uses except those of medicine, and for shipment is blasted off with dynamite and loaded into cars. Formerly, about 90 per cent of the sulphur used in the United States was obtained from Sicily. For pharmaceutic preparations further purification is deemed necessary. The sulphur

is placed in retorts and heated to the boiling point; its vapors pass over into chambers where condensation takes place upon the walls or coarse sacking. This is in the form of a fine powder, known as *flowers of sulphur.* If the process be continued for considerable time, the walls become sufficiently warm to melt the sulphur again and it runs to the bottom and is drawn off into moulds, in which form it is called *brimstone* or *roll sulphur.*

3. **Physical Characteristics.**—Sulphur is a solid of light yellow color. It is not soluble in water and is without odor or taste. It has a specific gravity about twice that of water and a melting point about 114. Its

Fig. 51.—Sulphur crystals.

best solvent is carbon disulphide in which at ordinary temperatures about 40 parts will dissolve in 100. If this solution be allowed to evaporate slowly, as may be secured by tying two or three thicknesses of filter paper over a beaker half or two thirds filled with the solution, a mass of beautiful crystals may be obtained such as are shown in Fig. 51. They are of the same shape as those found in nature but usually somewhat more perfect. They are called *orthorhombic* or *octahedral crystals.* Sulphur also forms long, needle-like crystals, known as *monoclinic.* These may be obtained by melting a quantity of sulphur in a beaker or large test tube and pouring upon a filter paper in a funnel. In a short time the needles will be seen growing rapidly across the surface of the molten sulphur. At this stage the portion remaining

molten should be poured out, after which the crystals may be easily examined. The two varieties are of the same color, but in many respects are as dissimilar as oxygen and ozone. Monoclinic sulphur has a specific gravity of 1.96, while that of the orthorhombic is 2.06; the former, a melting point of 119, the latter about 114; below 96° C. the needles break up into the orthorhombic. Hence, while a roll of sulphur recently made would consist of a mass of needle-like crystals closely intermingled, after a time these would have broken up into small octahedrons. On the other hand, if the orthorhombic variety be heated above 96° C. but not to the melting point, it slowly changes into the monoclinic variety. Sulphur brought to the boiling point and cooled suddenly, by pouring into water, forms another variety known as *plastic* or *amorphous* sulphur. This is very dark brown in color and at first is soft and elastic and is not soluble in carbon disulphide. In a few days it loses its dark color, and becomes hard and brittle. It is beginning to change back to the more stable variety. The process is very slow and may continue for years without completion. If put into water and kept at a temperature of 100° C. for about an hour, the change is complete. In heating sulphur to the boiling point, it is first a clear, golden-yellow, mobile liquid. As the temperature rises it becomes brownish in color, growing gradually more viscous till it cannot be poured from the vessel containing it. At the boiling point, about 448°, it is again a thin liquid nearly black in color.

4. **Chemical Characteristics.**—Sulphur above its kindling temperature reacts easily with oxygen, forming the dioxide. At red heat it combines vigorously with both copper and iron with the formation of sulphides. Sulphur vapor at a temperature not far above its boiling point shows a density indicating a molecular formula of

$S_8$; but like iodine and nitrogen peroxide, already studied, as the temperature rises, the expansion of the gas and the specific gravity change much more rapidly than justified by Charles' law, and at 800° the molecular weight indicated is about 64, which is that demanded if the formula is $S_2$. This gives another illustration of dissociation by heat,

$$S_8 \rightleftarrows 4S_2.$$

5. **Uses of Sulphur.**—While no longer used as extensively as formerly in medicine, sulphur still enters into a number of pharmaceutic preparations. It is mildly germicidal and is employed in some ointments for this reason. It is used extensively in viticulture in sprays to prevent the destructive effects of fungous diseases as well as upon rose bushes for the same reason. Boiled with lime it is used upon peach, plum and other fruit trees to prevent "brown rot," a disease of fungous character. Very considerable amounts are used in the manufacture of matches, gunpowder and fireworks. One of the most extensive uses is in the manufacture of rubber goods. Without the addition of sulphur, native rubber becomes unduly soft in warm weather and brittle in cold. *Vulcanite* is hard rubber, obtained by heating ordinary rubber out of contact with the air to a considerably higher temperature. This form is familiar in phonograph records, combs, telephone receivers and mouthpieces, electric insulation, fountain pens, and a great variety of other things. Lampblack is added in small amounts to give a black color: if pink is desired, vermilion is used. Considerable sulphur is used in the manufacture of such compounds as carbon disulphide and sulphur dioxide. The former is a nearly colorless liquid of very unpleasant odor as usually obtained, and employed largely as a solvent for various substances.

6. **Compounds.—Sulphides.**—Sulphur and oxygen being members of the same family show much similarity in the compounds they form. Oxygen unites with all the common elements except fluorine; so sulphur forms compounds with all the metals except gold and platinum and with a very large number of the nonmetals. Nearly all the metals occur in nature as sulphides.

7. **Hydrogen Sulphide.**—In nature hydrogen sulphide is often found in spring and artesian well waters. Eggs, which are proteins containing sulphur, in decomposing produce quantities of hydrogen sulphide, familiar to all in the exceedingly disagreeable, nauseating odor. In the laboratory it is obtained by treating ferrous sulphide either with hydrochloric or sulphuric acid, considerably diluted, thus,

$$FeS + H_2SO_4 \rightarrow H_2S + FeSO_4.$$

It is a colorless gas, a little heavier than air, with the well-known offensive odor of decomposing eggs. It is somewhat soluble in water with which it forms an acid solution, *hydrosulphuric* acid. It may be liquefied at about −60°. Hydrogen sulphide burns with a pale-blue, hot flame with the characteristic odor of burning sulphur. The equation is

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2.$$

If a cold dish be held against the flame, a deposit of sulphur is formed. This shows that by the heat present the escaping hydrogen sulphide is dissociated to a greater or less extent, thus,

$$2H_2S \rightleftarrows 2H_2 + S_2.$$

It is a very poisonous gas, producing dizziness, unconsciousness, and ultimately death. However, as at least

½ of 1 per cent is necessary for fatal results, and as very much smaller proportions than this are distinctly noticeable on account of its very strong odor, serious results very rarely occur. It is said that very dilute chlorine, obtained by adding hydrochloric acid to bleaching powder solution, is the best antidote. It must be remembered, however, that chlorine is more poisonous than hydrogen sulphide; hence, when used as an antidote, great care must be exercised. Like carbon and carbon monoxide, hydrogen sulphide is a reducing agent. Hence, when bubbled through strong sulphuric acid, partial reduction of the acid results with the formation of sulphur dioxide, thus,

$$H_2SO_4 + H_2S \rightarrow S + SO_2 + 2H_2O.$$

Hydrogen sulphide, therefore, cannot be dried by this method. Brought into contact with sulphur dioxide, a similar reduction takes place with the precipitation of free sulphur, thus,

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S.$$

This probably accounts in part at least for the deposits of sulphur in volcanic regions, as both the sulphide and oxide are produced by the action of heat upon compounds present in the earth.

Dissolved in natural water, artesian or spring, hydrogen sulphide is supposed to have therapeutic value, but this is very doubtful. In the laboratory, however, it is indispensable. It serves as the means of separating a large number of the metals into groups as the starting point of most chemical analyses.

8. **Sulphur Dioxide.**—There are two oxides, sulphur dioxide and trioxide, but the former is the more common. It is produced when either sulphur or hydrogen sulphide is burned in the air. In the laboratory it is

generally prepared by treating copper turnings or bits of charcoal with concentrated sulphuric acid, heated cautiously but somewhat strongly. It might be supposed at first thought that copper added to sulphuric acid would cause an evolution of hydrogen as zinc did. It will be found, however, by referring to Fig. 14 on p. 65 that copper is less strongly electropositive than is hydrogen, hence could not displace the latter from an acid. Moreover, we have seen that concentrated sulphuric as used in this case gives but few hydrogen ions, and as chemical changes are usually between ions, a reaction similar to that between zinc and dilute sulphuric acid could not be expected here. Thus with zinc we had

$$Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4.$$

Concentrated sulphuric acid, when heated, is an oxidizing agent, that is, it gives up a part of its oxygen; in other words, in the present case the copper serves as a reducing agent in its reaction with sulphuric acid. It is not possible to prove that a certan chemical reaction takes place by steps, still it is entirely possible that in this case as in many others, such is true. On the above supposition, the first step in the reaction would be shown by the equation,

$$Cu + H_2SO_4 \rightarrow CuO + H_2O + SO_2.$$

Then, secondly, $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$.
Adding the two equations gives the final result as it is known to be,

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2.$$

9. **Characteristics of Sulphur Dioxide.**—Sulphur dioxide is a colorless gas with a very suffocating odor. It is one of the easiest gases to liquefy; this may be accomplished in any laboratory by surrounding a spiral

tube connected with the sulphur dioxide generator with a freezing mixture of ice and salt. The liquid may be kept sealed hermetically in glass tubes, as the pressure at ordinary temperatures is only about three and a half atmospheres. The liquid if pure is nearly colorless, like water, and boils at −8° C. The gas is soluble in water to the extent of about fifty volumes in one and forms the unstable sulphurous acid, $H_2SO_3$,

$$SO_2 + H_2O \leftrightarrows H_2SO_3.$$

It has a density compared to hydrogen of 32, hence is nearly two and a half times as heavy as air. Being an unsaturated compound, since the valence of sulphur is six, it has the power of taking up another atomic weight of oxygen for each molecule, and thus forms sulphur trioxide.

10. **Uses of Sulphur Dioxide.**—Until comparatively recent years sulphur dioxide was used for disinfecting public buildings and homes in case of contagious diseases. The gas was secured by burning sulphur "candles" in the various rooms or where the ventilating fans would carry it to all parts of the building. As formaldehyde is much more effective and more easily obtained it is largely supplanting sulphur dioxide for fumigating purposes. It is used extensively for bleaching various food products, as, for example, glucose syrups, already mentioned; also, for freshly cut fruits in drying. The fruit is peeled, cored and sliced, by machine at a single operation, and the slices spread upon trays over a furnace in an evaporator. A teaspoonful of sulphur is put into a cup on top of the furnace each time a double tray of fruit is inserted. The sulphur burns, forming sulphur dioxide, and the gas flows up over the fruit. No brown discoloration occurs as would be the case in pure

air, and in a very few minutes the fruit is dry upon the surface after which it remains perfectly white. In many localities in the West, fruits, especially peaches and apricots, are dried in the sun. To prevent attack by ants and other insects, the fruit after being cut is taken to a "sulphuring" room where it is exposed to sulphur dioxide fumes for a time. Sufficient is absorbed to protect the fruit in drying; however, at the temperature present, as the water evaporates, the sulphur dioxide, except in minute traces, also disappears, so that no harmful results follow. The bleaching of English walnuts and almonds, possibly of some other nuts in California, is a common practice. Lying upon the ground in the "hulls" as they may for some days before being gathered, the white shells become stained or mildewed, so that when finally shelled and dried they are of varying shades of brown and gray. When taken to the packing houses, after being assorted into sizes, they are passed through a solution of bleaching powder to which dilute hydrochloric acid has been added, then carried by elevators to a "sulphuring" room, where they are exposed for some time to the fumes of sulphur dioxide. The result is a product with shells of a uniformly creamy-white color. They are thus rendered pleasing in appearance without detracting from the wholesome character of the nuts.

Liquefied sulphur dioxide is now an article of commerce and is used extensively for bleaching woolens, straws and silks. Naturally, these articles are all of varying shades of yellow and woven thus are unattractive in appearance. Chlorine is destructive of all such and cannot be used. Sometimes hydrogen peroxide is employed, but it is not so satisfactory as sulphur dioxide. What the chemical action is when bleaching is

done with this gas is uncertain. The other two bleaching agents already studied undoubtedly act by oxidation. As sulphur dioxide is an unsaturated compound it would presumably act by reduction of the colored compounds in the fabric to colorless. All such articles, on exposure to air and sunlight, again become yellow, caused possibly by their again taking up oxygen and returning to their first condition. Iceless refrigerators kept cold by the evaporation of liquid sulphur dioxide are now being installed in many homes. The principle is the same as already explained in the manufacture of ice.

11. **Sulphur Trioxide.**—This oxide has little interest outside the fact that it is the anhydride of sulphuric acid. It will be taken up in connection with the preparation of that acid.

12. **Sulphurous Acid.**—As already stated this acid is formed when sulphur dioxide is passed into water. It is unstable and of little importance.

13. **Sulphuric Acid.**—Under the name, *oil of vitriol,* sulphuric acid has been known for centuries. It was formerly made, somewhat impure, by distilling ferrous sulphate, called green vitriol, which gave the name to the acid. At the present time two methods are used in its manufacture, the *chamber* and the *contact process.* The former is the older method, but the latter, where it may be applied is the cheaper. Both employ sulphur dioxide as the starting point.

14. **The Chamber Process.**—By this method the sulphur dioxide needed is usually obtained by roasting iron pyrite, $FeS_2$, which reacts with the oxygen of the air thus,

$$4FeS_2 + 11O_2 \rightarrow 8SO_2 + 2Fe_2O_3.$$

The gas is passed into large chambers where it meets

nitric acid vapors prepared by the action of sulphuric acid upon sodium nitrate, thus,

$$2NaNO_3 + H_2SO_4 \rightarrow 2HNO_3 + Na_2SO_4.$$

The nitric acid and the sulphur dioxide react, with the formation of sulphur trioxide and one or more nitrogen oxides,

$$2HNO_3 + 3SO_2 \rightarrow 3SO_3 + H_2O + 2NO.$$

Steam and currents of air are also introduced by which the sulphur trioxide forms sulphuric acid and the nitric oxide becomes peroxide, thus,

$$H_2O + SO_3 \rightarrow H_2SO_4.$$
$$2NO + O_2 \rightarrow 2NO_2.$$

Only small quantities of nitric acid are needed, since it serves merely as a catalytic agent to transfer the oxygen from the air to the sulphur dioxide. However, as four-fifths of the air is nitrogen which has no use in this process, in removing it special plans must be adopted to prevent loss of the nitrogen oxides also. The escaping gases are made to pass up through what is called the Gay-Lussac tower, little more than a chimney with a lattice work of brick or tile, over which sulphuric acid slowly trickles. This acid has the power of combining with the nitrogen oxide present but not with the nitrogen, and forms what is called *nitre* acid or *nitrosyl sulphuric* acid. Thus, little of the nitric oxide is lost. The nitrosyl sulphuric is then pumped up to the top of another chimney known as the Glover tower and trickling down there meets the steam and fresh supplies of sulphur dioxide. The steam decomposes the niter acid forming sulphuric and sets free the nitric oxide which again combines with the oxygen of the air; hence the process becomes continuous. The chambers where the acid is pro-

duced are lined with lead, since it is not attacked by dilute sulphuric. When it reaches a strength at which it begins to react with the lead, it is removed and further concentrated in stills made of cast iron or platinum. (See Fig. 52.)

15. **The Contact Process.**—This process uses platinum as the catalytic agent. It is found that sulphur dioxide and air, mixed and passed through a heated tube, do not react to any appreciable extent. If finely divided

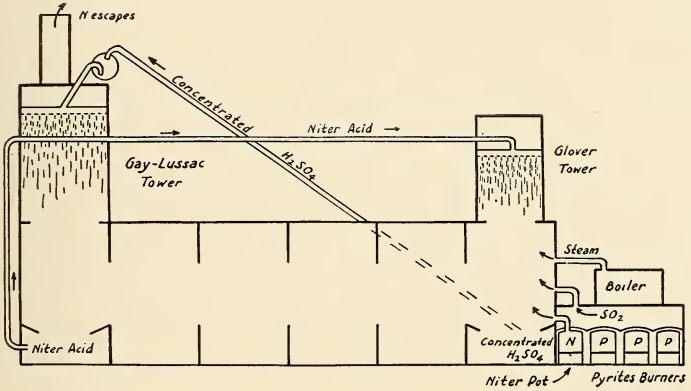



Fig. 52.—Chamber process for sulphuric acid. The escaping gases pass up the Gay-Lussac tower where they meet the streams of sulphuric acid. This combines with the nitrogen oxide present, forming the niter acid, so called. This is pumped to the top of the Glover tower, where, descending, it meets the steam, which decomposes it. The nitrogen oxide then begins its work all over again.

platinum be present, however, the union is rapid. In preparing the catalyzer, asbestos is dipped into a solution of platinum chloride and heated. The chlorine is expelled and the finely divided platinum is left adhering to the surface of the asbestos. When this is heated and the mixed air and sulphur dioxide passed through it, sulphur trioxide is formed, which though a solid, is vaporized by the heat present and passes out of the

catalyzer into a receiver containing moderately dilute sulphuric acid, such as is obtained by the chamber process. This continues till the liquid becomes a white crystalline solid, known as fuming sulphuric acid, with the formula, $H_2S_2O_7$, or $H_2SO_4.SO_3$. This indicates it is sulphuric acid saturated with the anhydride, sulphur trioxide. It might be supposed that the sulphur trioxide obtained by the contact process would be passed directly into water, rather than into dilute sulphuric acid. The reason that this is not done is that the reaction is so violent that the heat produced volatilizes considerable portions of the trioxide with much loss.

16. **Characteristics of Sulphuric Acid.**—When pure, sulphuric acid is a colorless, oily liquid, with a specific gravity of 1.84. It boils at 330° C., but considerable portions are broken up into sulphur trioxide and water, thus,

$$H_2SO_4 \rightleftarrows SO_3 + H_2O.$$

Sulphuric acid is strongly hygroscopic and exposed to the air rapidly increases in volume with corresponding dilution. When water is added, great heat is produced; hence, it is never safe to pour water into the concentrated acid. The reverse order should always be followed. As already seen, this strong attraction for water is made use of in drying gases. When a pine splinter is dipped into concentrated sulphuric acid, it is charred, as is also a lump of sugar. From the former, being largely cellulose, $C_6H_{10}O_5$ the acid removes the hydrogen and oxygen as if it were water, leaving the carbon behind. The same is true of the sugar. In the diluted form sulphuric acid is largely ionized, hence is a good conductor of electricity, and with any metal more positive than hydrogen readily reacts, giving off the hydrogen. In concentrated form there are very few ions pres-

ent; it is then a very poor conductor and with such metals as zinc and iron its reaction is very slight.

17. **Uses.**—This is the most extensively employed of all acids. It is used in the preparation of all other acids; the method for hydrochloric and nitric we have already seen. It is used in the manufacture of explosives such as nitroglycerine and guncotton, for the preparation of fertilizers from native phosphate rocks, in refining oils derived from petroleum and in the preparation of coal tar dyes.

18. **Thiosulphuric Acid.**—This acid has never been prepared but its salts are well known. It has the formula, $H_2S_2O_3$, which will be seen to be sulphuric with one of the atoms of oxygen replaced by one of sulphur. The first part of the word, *thio,* is from the Greek word for sulphur, and is given to this acid to indicate the fact of the substitution of the sulphur for the oxygen. One salt of this acid, sodium thiosulphate, is very important. It is sold under the name "hypo," formerly erroneously called hyposulphite of soda. It is used extensively in photography in "fixing" plates and prints so that they will not be further acted upon by the light. It is also used as an *antichlor* in the bleaching of textile fabrics to remove the last traces of the chlorine, so as to prevent its attacking the cloth. The fact that it was used during the later part of the war in gas masks has been mentioned elsewhere.

### Exercises for Review

1. Name three localities where sulphur is found very abundantly. In what condition is it and how situated?

2. Give the method of obtaining the supply used in the United States.

3. Name four varieties of sulphur and state how each may be obtained.

4. Give some important differences between the two crystalline varieties.

5. Give the chief physical characteristics of sulphur. How does the amorphous differ from the yellow?

6. What is an allotrope? What other substances have we met with in allotropic forms?

7. Give the chief chemical characteristics of sulphur.

8. Give some very important uses of sulphur. What is vulcanite? Uses.

9. Where is hydrogen sulphide found in nature? Give some of its properties.

10. Write the equation showing the combustion of hydrogen sulphide. Why cannot it be dried by sulphuric acid as many gases are?

11. What is meant by reduction? When hydrogen sulphide and sulphur dioxide are mixed, which is reduced, which is oxidized? Is it possible to reduce one substance without oxidizing another.

12. Name the oxides of sulphur and give their formulas.

13. How is sulphur dioxide prepared in the laboratory? How for fumigating? Why is hydrogen not obtained from the sulphuric acid by copper?

14. Give the chief properties of sulphur dioxide.

15. Name the most important uses of sulphur dioxide.

16. Name two other bleaching agents previously studied. For what are they used to bleach?

17. Give the names of two processes for making sulphuric acid. How did it come to be called "oil of vitriol"?

18. Describe briefly the chamber process and write the equations.

19. Describe briefly the contact process. What is the catalytic agent in each process?

20. Describe the sulphuric acid and give some important uses.

21. Why does a lump of sugar in concentrated sulphuric acid turn black?

22. What is the action of sulphuric acid in making nitrocellulose?

23. For what is hypo used? What is its chemical name?

# CHAPTER XXII

## PERIODIC CLASSIFICATION OF ELEMENTS

**Outline—**

Comparison of Metals and Nonmetals
Atomic Weight and Chemical Characteristics
The Periodic Table
Valence in the Table
Relation of the Properties to Position in Table
Group Characteristics
Numerical Relations
Characteristics of Compounds as Related to Position

1. **Classification of the Elements.**—Heretofore we have spoken of the elements as metals and nonmetals. Most of the common metals are of considerable density and lustrous; but sodium and potassium are both so light as to float on water, yet are decidedly metallic in characteristics. Arsenic has a bright, metallic luster, yet can hardly be called a true metal. We have spoken of the metals as forming electropositive ions and the nonmetals, electronegative: in a general way this is true, yet many of the metals are found in complex electronegative ions. Aluminum and tin are both metals, yet well known salts exist in which with oxygen these metals constitute the negative ion. Likewise some nonmetals may form positive ions. The metals have been spoken of as forming basic oxides and the nonmetals as anhydrides. Generally speaking, this is true. However, zinc hydroxide, $Zn(HO)_2$, and aluminum hydroxide, $Al(HO)_3$, are both soluble in sodium hydroxide, which indicates that the two bases must have ionized as if they were acids, thus,

$$H_2ZnO_2 \rightleftarrows \overset{+}{H}\overset{+}{H} + Zn\overset{-}{O}_2\overset{-}{,}$$

$$H_3AlO_3 \rightleftarrows \overset{+}{H}\overset{+}{H}\overset{+}{H} + Al\overset{-}{O}_3\overset{-}{.}$$

This must be true for the salts formed are $Na_2ZnO_2$ and $Na_3AlO_3$, sodium zincate and sodium aluminate. It is seen, therefore, that there are many exceptions to the general statements regarding the two divisions of elements hitherto used, such that this method of classification is far from satisfactory.

2. **Classification by Atomic Weights.**—For long years there have been chemists who believed that the characteristics of an element bore some close relation to and are dependent upon its atomic weight. Various attempts were made to show this, but too many facts were unknown for any marked success. It remained for a great Russian chemist who died in 1907, to prepare what is known as the "Periodic Table" and to present the "Periodic System" in such a way as to cause its acceptance by chemists at large. Starting with the idea that the properties of an element are a function of the atomic weight, Mendeléeff arranged the elements in the order of their atomic weights, beginning with the lightest, but omitting hydrogen. In this way he had lithium, glucinum, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminum, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and so on. By inspecting this arrangement he discovered that leaving lithium, there is no other element similar to it until sodium is reached in the eighth space beyond, and then potassium another octave beyond the sodium. Starting with fluorine, no other element is met similar to it until chlorine is reached, the eighth beyond. Observing this fact in many instances, he next attempted to arrange the elements known to him into *octaves,* putting like elements

under each other. To make the elements known at that time agree with his theory, he was compelled to leave many spaces in the table he prepared blank. But in doing so he predicted these spaces would be filled in the years to come; what is more, he even foretold the general properties these unknown elements would possess, their approximate atomic weights, and, in some instances, actually suggested names for them. Most of his predictions have since that time been fulfilled, although the names he suggested have not been accepted. The latest form of the table, with some omissions as noted, as well as of some very rare elements whose position as yet is not determined, is given on page 268.

Only a very brief study of the table is possible at this time, but some knowledge of it is necessary and will be found very helpful to the student. Let it be remembered that the basis of arrangement is the *atomic weights* of the elements.

3. **Valence in the Table.**—The vertical divisions in the table are called *Groups* and the horizontal divisions, *Periods*. By looking at the top of each group, beginning with lithium, it will be seen that the valence increases from *one* up to *seven*. This is true for each period, with few exceptions which will be noticed. It is based upon the oxides which the elements form. For example, taking the second period, the respective oxides have the formulas, $Na_2O$, $MgO$, $Al_2O_3$, $SiO_2$, $P_2O_5$, $SO_3$, $Cl_2O_7$. The next period, if the oxides are taken, shows the same valence, and so on through the table. If the hydrogen compounds are considered after the carbon group is passed, in which the valence is four, the apparent value decreases by one at each group. Thus, we have the formulas for the four compounds, marsh gas, ammonia, water and hydrogen chloride, $H_4C$, $H_3N$, $H_2O$, $HCl$. The following

| VALENCE = 0 NO COMPOUNDS | VALENCE = 1 | VALENCE = 2 | VALENCE = 3 | VALENCE = 4 | VALENCE = 5 IF SATURATED | VALENCE = 6 IF SATURATED | VALENCE = 7 IF SATURATED |
|---|---|---|---|---|---|---|---|
| He,4 | Li,7 | Gl,9 | B,11 | C,12 | N,14 | O,16 | F.19 |
| Ne,20 | Na,23 | Mg,24.3 | Al,27 | Si,28 | P,31 | S,32 | Cl,35.5 |
| A,39.9 | K,39 | Ca,40 | Sc,44 | Ti,48 | V,51 | Cr.52 | Mn,55 |
| ..... | Cu,63.6 | Zn,65.4 | Ga,70 | Ge, 72.5 | As,75 | Se,79.2 | Br,80 |
| Kr,83 | Rb,85.4 | Sr,87.6 | Y,89 | Zr,90.6 | Cb,93.5 | Mo,96 | ..... |
| ..... | Ag,108 | Cd,112.4 | In,115 | Sn,119 | Sb,120 | Te,127.5 | I,127 |
| Xe,130 | Cs,133 | Ba,137.4 | La,139 | Ce,140 | Ta,181.5 | W,184 | ..... |
| ..... | Au,197 | Hg,200.6 | Tl,204 | Pb,207 | Bi,208 | ..... | ..... |
| Nt 222.5 | ..... | Ra,226.5 | ..... | Th,232.5 | ..... | U,238.5 | ..... |

In addition to the elements shown in the table there are three groups which do not seem to "fit" anywhere. Thus following manganese, are iron, nickel, cobalt, with weights of 56, 58.7 and 59 respectively; following the blank space below manganese, ruthenium, 102, rhodium, Rh, 103, and palladium, 107; following the blank after tungsten, W, are osmium, 191, iridium, 193, platinum 195.

periods show like valence with the hydrogen compounds. When Mendeléeff first prepared the table no element of the first column had been discovered and he made no plans for any such group. But strange to say, and wonderfully strengthening the probable truth underlying his plan, when the argon group was discovered one by one, with a slight exception to be noted, they all fitted into the general plan and no changes had to be made. Singularly, too, their valence is *zero,* that is they have no power of combining with other elements and as far as discovered form no compounds whatever. The slight exception to be noted is that argon as thus far prepared is slightly heavier than potassium, whereas it should be lighter. The probable explanation is that the argon thus far obtained is not pure but contains small quantities of one or more of the heavier gases belonging to the same group. It will be remembered that for years this was found true of the nitrogen obtained from the air; and the fact of its unseeming density when thus prepared led to the discovery of argon. One other exception which might be mentioned here is that iodine is slightly lighter than tellurium, whereas the reverse should be true. It is generally believed that the weight of the iodine will sometimes be found to be slightly incorrect. Constant efforts are being made to ascertain whether this may not be true.

4. **Position of the Elements and Properties.**—It will be found that as we go from left to right in the table, omitting always the argon group, the elements become less and less electropositive and passing the carbon group, become more and more negative. Thus, sodium is very strongly positive while chlorine is equally strongly negative. Sodium forms a very strong base, chlorine a very strong acid. Taking the right hand end of the table it will be found, as we go down the

group, that with the increasing weight the elements become less and less acidic in properties and begin to have some of the physical properties of the metals. Thus, in the halogen group, iodine is solid in form and has a luster, closely resembling that of most metals. In the nitrogen family the lightest one is a gas, phosphorus is a waxy solid, arsenic a brittle solid, but lustrous, antimony decidedly metallic in appearance but with some chemical properties of an acidic element, while bismuth, the heaviest, is a metal both in appearance and behavior. Hence, instead of dividing the table into positive and negative elements by a vertical line near the center, it must be done by an irregular, or zigzag diagonal, starting at the left of boron, leaving it above and aluminum below the line, and so on through, leaving iodine above. Divided in this way the elements above the line generally speaking are electronegative or acid forming elements, while those below are positive or base forming elements. However, it must be further noted, that the elements near the irregular diagonal usually partake of a dual character and form both acids and bases, though weak ones. Thus aluminum, arsenic, antimony, tin and others less familiar to the student all serve both as acid- and base-forming elements at different times.

5. **Group Characteristics.**—Taking any particular group for study it is found that all the members possess the same general characteristics and form similar compounds. We have thus noticed two members of the sodium group. Both are silvery white metals, light enough to float on water, decompose it readily even in the cold, are strongly caustic and form strong hydroxides. Taking the chlorine group, it is found that they resemble each other equally strongly. So it is found

largely true throughout. Most strikingly is this observed in the chemical behavior and in the compounds formed. Thus, the sodium group forms no ordinary compounds of hydrogen for the reason that they are all strongly positive as is hydrogen also, but they do form oxides of the type, $Na_2O$. The halogens form acids after the type, HCl. The sulphur group forms compounds with hydrogen seen in the formulas, $H_2O$, $H_2S$, $H_2Se$, $H_2Te$ and with the oxides whose formulas are $SO_3$, $SeO_3$, $TeO_3$. The nitrogen family forms hydrogen compounds shown in the formulas, $NH_3$, $PH_3$, $AsH_3$, $SbH_3$ and oxide compounds in $N_2O_5$, $P_2O_5$, $As_2O_5$, $Sb_2O_5$, $Bi_2O_5$. Hence, having learned the characteristics and compounds of one member of a group, we may know, in a measure that the same things are true of other members of the same group.

6. **Numerical Relations.**—It was stated that Mendeléeff predicted with approximate accuracy the atomic weights of the unknown elements. By observation it will be seen that the atomic weight of any element is roughly speaking the arithmetic mean of those of the two adjacent elements. To illustrate: Sodium, weight 23, is one-half the sum of 7 and 39, the weights of lithium and potassium; scandium, weight 44, is half the weight of calcium and titanium, 40 and 48. Thus it is all through the table, although not always as exact as in these two cases; but the variation is not great.

7. **Characteristics of Compounds Formed.**—In a general way the character of the compounds may be known somewhat from the position of the elements forming them. Thus, nearby elements, possessing similar characteristics would not be expected to unite to form compounds at all. In the case of the metals, most of the *unions* formed are not true compounds. With the non-

metals, such as nitrogen and oxygen, nitrogen and chlorine, and others, when such do form compounds it is usually through indirect processes by which the two elements are *left* together and such compounds are very unstable. The oxides of nitrogen already studied, are all more or less unstable; further, it has been noted that practically all the explosives are compounds of nitrogen and oxygen and owe their explosive properties to the instability of such compounds. Chlorine and oxygen form oxides, indirectly, but they are dangerously explosive, as are also those of nitrogen and chlorine. On the other hand, elements distantly located in the table form very stable compounds. Thus, sodium and chlorine, or calcium and fluorine, unite readily and directly and form relatively very stable compounds. Such are a few of the more important facts regarding the periodic table. From this time forward the various elements studied will be taken up in accordance with the "Periodic System" or arrangement, as shown in the table.

### Exercises for Review

1. What two divisions of the elements have been used thus far? Give some of the general characteristics of each division.

2. What objection is offered to this as a scientific method of classification?

3. What is the basis of arrangement in Mendeléeff's table? How did he come to discover the recurrence of properties?

4. What arrangement was made of the elements after the recurrence of properties was observed?

5. What is a group in the table? A period?

6. State what is observed regarding valence in the table, using both the oxygen and the hydrogen compounds. What is the valence of the argon family? What is meant by that statement?

7. State what is observed in passing from left to right in a period.

8. What is true in each group at the right side of the table as the weight increases?

9. Where does the dividing line come in the table? Give the general characteristics of the elements on either side of the line.

10. What may be said of the elements close to the diagonal on either side? Illustrate.

11. What is true of the general characteristics of the elements in any particular group? Illustrate by taking some family as that of sulphur or chlorine.

12. What numerical relation exists among the elements? Take the entire first period and show this.

13. What would be the approximate weight of the unknown element belonging in the space below cæsium, in the sodium family? At the right of radium? At the right of molybdenum?

14. What is generally true of compounds formed from elements near each other in the table? Illustrate.

15. What is true of compounds formed from distantly placed elements? Illustrate.

16. Why should arsenic be expected to have both basic and acidic properties? Which would be the more pronounced?

17. Would you expect to find zinc with any acidic tendencies? If so, how would they compare with those of aluminum?

18. Noting the fact that hydrogen and bromine are close to the diagonal, what would you expect to be true of the stability of hydrogen bromide as compared with hydrogen chloride? What of hydrogen iodide? What does our work in bromine show?

19. Ought chlorine to displace bromine from a compound or the reverse? How about chlorine and iodine?

# CHAPTER XXIII

## THE NITROGEN FAMILY

**Outline—**

Members of the Group

Phosphorus

(*a*) Occurrence
(*b*) Preparation
(*c*) Forms of
(*d*) Characteristics
(*e*) Uses—Poisons
Matches
(*f*) Hydrogen Compound
(*g*) Oxides
(*h*) Phosphates
(*i*) Fertilizers

Arsenic

(*a*) Occurrence
(*b*) Characteristics
(*c*) Uses
(*d*) Arsine
(*e*) Tests for
(*f*) Oxides of
(*g*) Antidote for Poisoning
(*h*) Pigments

Antimony

(*a*) Characteristics
(*b*) Uses
(*c*) Stibine
(*d*) The Sulphide
(*e*) Tartar Emetic

Bismuth

(*a*) Characteristics
(*b*) Uses
(*c*) The Nitrates

Tabular Comparison of Compounds

1. **Members of the Family.**—Nitrogen, the lightest, has already been studied in connection with the atmosphere. The other members are phosphorus, arsenic, antimony and bismuth. These four are all solids, and the last three, while not strikingly alike in some of their physical properties when untarnished, closely resemble each other in their bright metallic luster and crystalline appearance; but it is in the compounds formed and the chemical behavior in which they agree most closely.

2. **Phosphorus.**—Phosphorus was discovered as long ago as 1669. About a century later, 1771, Scheele prepared it from bone-ash, a plan which has been followed nearly ever since. The word phosphorus means *light-bearer*, and was given to the element because of the fact that it glows in the dark when exposed to the air. In the form of a phosphate rock, calcium phosphate, it occurs abundantly in some of the Southern States, especially Florida, South Carolina and Tennessee. It is found in small quantities in the nerve centers and muscles of the body, but more largely in the bones, of which, as calcium phosphate, it constitutes about three-fifths in weight. In the average human body it is said that there are about 3 pounds of phosphorus, nine-tenths of which is in the bones and most of the remainder in the muscles.

3. **Preparation of Phosphorus.**—Up to recent years the bones of cattle, obtained from the packing houses, from which the gelatine and oil had been extracted, were charred to form bone charcoal. When this was no longer valuable for refining sugar, it was burned to a white ash in the air and from this calcium phosphate the phosphorus was distilled. At the present time, native phosphate rock, supposedly the fossil remains of birds, is mainly employed. With the crushed rock are mixed sand and coke or charcoal, the mixture is fed into an

electric furnace by a worm drive below the hopper, as shown in Fig. 53. When strongly heated the carbon removes a portion of the oxygen, while the sand forms a slag with the calcium and is drawn off at the bottom. The phosphorus, thus set free, distils out in the form of vapor, is condensed under water, and molded into small sticks.

4. **Forms of Phosphorus.**—Similar to several other elements already studied, especially, oxygen, carbon and sulphur, phosphorus occurs in two distinct varieties.

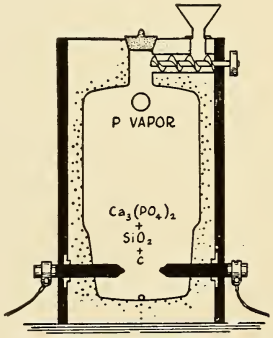



Fig. 53.—Manufacture of phosphorus.

Prepared, as described above, it is known as *yellow* phosphorus; if this be heated to a temperature of 250° C. out of contact with the air *red* phosphorus is obtained.

5. **Physical Characteristics.**—Yellow phosphorus, when freshly prepared or when first opened from a "tin" container which has excluded all light, is of a very pale-amber color, so nearly colorless, that it is sometimes called *white* phosphorus. It is of waxy appearance when cut. On exposure to light it deepens in color, owing to the formation of a coating of the red variety. The yellow is soluble in carbon disulphide, and taken internally is

very poisonous. The vapors, continually inhaled, are also poisonous, and produce a disease of the jaw bones, known locally as "phossy jaw," which may be relieved only by surgical operation and generally is incurable. The molecular weight of phosphorus vapor is 128, which indicates four atoms to the molecule, formula $P_4$. Red phosphorus is a dark reddish-brown powder, not soluble in carbon disulphide. It is not poisonous and need not be kept in water as must the yellow. If vaporized at a temperaure of 300 it changes to the yellow variety; that is, the vapor from both the red and yellow varieties is the same and upon being condensed forms the unstable variety.

6. **Chemical Properties.**—Yellow phosphorus, exposed to air, glows in the dark; in contact with chlorine it catches fire instantly; with liquid bromine, and after a few seconds with iodine, it does the same. If ignited, both varieties burn in oxygen with great brilliance. It is singular, however, that in a jar of oxygen, phosphorus does not glow at ordinary temperatures. If a solution of phosphorus in carbon disulphide be put upon two strips of blotting paper and inserted, one into a bottle of oxygen and the other into one of air, the latter will ignite as soon as the solvent has evaporated. The other remains unaffected unless the bottle be opened to the air when ignition takes place only after from one to three minutes have elapsed.

7. **Uses.**—Yellow phosphorus in small quantities is used in poisons for rats, mice and similar vermin. Most of it, however, is employed in the manufacture of matches. The original sulphur match was made by dipping pine splints into molten sulphur, and then adding a mixture of phosphorus in glue. Friction exposed the phosphorus and ignited it, whereupon, the sulphur, of

low kindling point, caught fire and in turn the pine splint. Such matches, while, vastly better than none or those that had preceded them, burn slowly and form considerable sulphur dioxide. On this account they fell into disfavor. To increase the speed of combustion some oxidizing material, like potassium chlorate or nitrate was added; instead of sulphur, the splints were dipped into melted paraffin for kindling. This gave a rapid match and a serviceable one, but dangerous. The mixture upon the head was too easily ignited; many fires were caused by the ordinary friction incident to their transportation. Moreover, owing to the amount of yellow phosphorus in their composition, not only were the workmen in the factories constantly subjected to the fumes, but children were often poisoned by them. These facts led to adverse legislation and in many states such matches were forbidden; then came matches of the "Birdseye" type, which contained phosphorus only in the tip of the head and which could not be ignited by friction on the sides. These did away with most of the fires, but not with the poisonous properties. Finally, the United States government by levying a direct tax of 2 cents per hundred matches legislated them out of existence. At present, ordinary matches are made by dipping the splints into melted paraffin for kindling, then into a mixture of some compound of phosphorus and some oxidizing material, as potassium chlorate, with dextrin or glue as the adhesive. The friction produced by "striking" the match is sufficient to decompose the phosphorus compound, ignite the phosphorus and then the kindling. The phosphorus compound used is not poisonous.

8. **Safety Matches.**—In this variety of match red phosphorus and antimony trisulphide mixed together are put

upon the box by means of a little glue: upon the splint is the paraffin for kindling, and antimony trisulphide with some oxidizing compound. Friction upon the prepared surface of the box vaporizes a small portion of the red phosphorus, the vapor is ignited and sets fire to the combustible material upon the splint. Such matches may be ignited upon other surfaces, not thus prepared, but a long stroke, with much friction is needed to produce sufficient heat to ignite the antimony compound which is combustible.

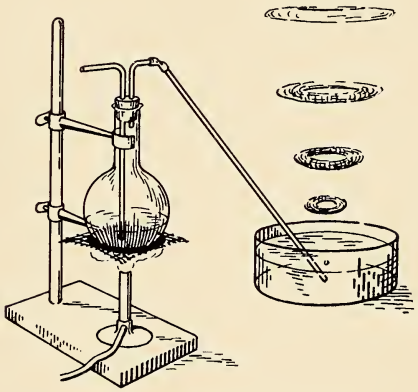


Fig. 54.—Preparation of phosphine.

9. **Phosphine.**—This compound is a gas made by the reaction of a solution of either sodium or potassium hydroxide upon yellow phosphorus. It is of interest because of the fact that as thus obtained it ignites spontaneously on exposure to the air. The following equation shows the chemical reaction,

$$P_4 + 3NaHO + 3H_2O \rightarrow 3NaHPO_2 + PH_3.$$

The reaction takes place at the boiling temperature, only slowly at room temperatures; the spontaneous ig-

nition is said to be due to the presence of a minute quantity of a liquid hydrogen phosphide, $P_2H_4$. If the gas be collected over water and allowed to stand thus for several hours, the liquid, $P_2H_4$, is dissolved and the gas does not ignite spontaneously. Apparatus such as was used for making hydrogen, may be used, except that the thistle tube should have substituted for it a piece of ordinary glass tubing bent at the upper end as shown in Fig. 54. This must reach to the bottom of the flask. Before applying heat the air must be removed; this is most easily done by attaching the gas supply to the bent tube and running the gas through for two or three minutes. The same should be repeated at the close of the experiment, otherwise as the air enters to take the place left by the contracting gas as it cools, it will cause an explosion. As the bubbles of phosphine come to the surface of the water in the trough they ignite spontaneously and in still air rings of white "smoke" float upward. The gas has no practical uses.

10. **The Oxides.**—Phosphorus forms two common oxides, the trioxide and pentoxide, $P_2O_3$, and $P_2O_5$, both produced by burning of phosphorus in the air. When the supply is plentiful, the higher oxide is obtained; when limited, the trioxide. They are both white solids and are the anhydrides of acids. Thus,

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3,$$
$$P_2O_5 + H_2O \rightarrow 2HPO_3.$$

The latter is very vigorous in chemical action such that when the oxide is dropped into water a hissing sound like that of a hot iron touching the water is heard. The acid produced is known as meta- or glacial phosphoric acid and corresponds to nitric acid, $HNO_3$. If the pen-

toxide is put into boiling hot water the reaction is different, thus,

$$3H_2O + P_2O_5 \rightarrow 2H_3PO_4.$$

This is known as orthophosphoric acid. Upon heating, it loses water and changes into the metaphosphoric.

11. **Phosphates.**—Salts of orthophosphoric acid are called phosphates. The most common are those of sodium, potassium and calcium. These are found in most soils in sufficient quantities for plant growth, but successive cropping, especially by various grains such as wheat or corn, remove them to such an extent that they must be replaced by fertilizers. The human body requires phosphates for the bones, muscles and nerve centers. This is obtained mainly through the cereal foods, although eggs, beans and peas also contain it.

12. **Fertilizers.**—The three things most needed for plants to insure vigorous growth and production of fruit or seed are nitrogen, phosphorus and potash. Means of procuring the nitrogen have already been studied. Two important sources of phosphates are the native rock already mentioned and bone products from the packing houses. Neither of these compounds is soluble in water and hence unavailable for plant food. However, if treated with sulphuric acid, they are converted into an acid phosphate, $CaH_4(PO_4)_2$, which is soluble in water and therefore suitable as a fertilizer. The reaction is shown thus,

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow 2CaSO_4 + CaH_4(PO_4)_2$$

Phosphorus-bearing iron ores are also a source of a considerable amount of the same acid phosphate, commercially known as the "superphosphate." It is said that in soils containing much humus the acids formed by the decomposition of the organic matter slowly convert native

phosphate into the superphosphate and thus make it available.

13. **Arsenic.**—This element, third in density in the nitrogen family, occurs in nature in arsenical iron pyrite $(FeAs)S$; also as realgar and orpiment, both sulphides of arsenic. The first named is the usual source of the commercial supply.

14. **Characteristics.**—Arsenic as obtained from the pyrite is of a dark gray color, and as usually seen, not lustrous. Upon heating in an open dish the dull coating disappears, leaving the element in its natural lustrous, steel-gray color. It vaporizes upon heating without melting, at a temperature of 180° C. The molecular weight of the vapor is 300 which is four times the atomic weight. This shows that the formula for the molecule, like that of phosphorus, is $As_4$. Powdered arsenic sifted into a jar of chlorine ignites spontaneously and burns as it falls; on bromine, it combines likewise with vigor. In the air it burns with a purplish white light and forms heavy white fumes of the trioxide, $As_2O_3$.

15. **Uses.**—There are few uses for the element. In the manufacture of shot from lead about 1 per cent of arsenic is added. The main reason for this is that the mixture of lead and arsenic is when molten much more limpid or mobile than pure lead. As a result, in pouring, the liquid is broken up the more easily and the shot are much more perfect. They are at the same time a shade harder than they would be otherwise. As the melting point of the mixture is lower than that of lead alone, solidification does not take place so rapidly, which gives the shot more time in assuming perfect spherical form.

16. **Arsine.**—As nitrogen and phosphorus form hydrogen compounds so does arsenic, with a formula corre-

sponding to that of ammonia and phosphine. It is usually prepared by adding to a hydrogen generator a solution of arsenic. It is usually not collected, but burned as generated. The equations show the chemical reactions taking place,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H,$$
$$AsCl_3 + 6H \rightarrow AsH_3 + 3HCl.$$

In the equation it may be noticed that the hydrogen was not written $H_2$ as has been done in previous cases, when it has been collected in the molecular condition. In

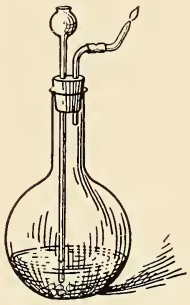


Fig. 55.—Marsh's test for arsenic.

the present instance it reacts with the arsenic as fast as it is set free from the acid and is said to be in the *nascent* condition. The term means *being set free.* In such condition it is much more active than in the molecular form. Some chemists offer a different explanation for the greater activity but the term is commonly used and should be understood. The arsine obtained thus always contains an admixture of hydrogen, but this does not interfere with the study of it.

17. **Characteristics.**—Arsine is a colorless gas with a somewhat offensive and nauseating odor. It may be

liquefied at −40° C. It is exceedingly poisonous, so that small quantities inhaled may result fatally. It is easily decomposed by heat as shown by the equation,

$$4AsH_3 \rightarrow As_4 + 6H_2.$$

This is easily shown experimentally. If a hard glass tube is attached to the arsine generator and a Bunsen flame is placed beneath the tube, the arsine is decomposed; and at a short distance beyond the heated portion a black ring of the arsenic appears, while the hydrogen escapes from the tube and may be burned. The plan is simplified oftentimes, as shown in Fig. 55, by holding a cold dish against a small arsine flame. Brownish black spots with metallic luster appear upon the dish. The explanation is the same as before; the vapor of arsenic obtained by the dissociation of the arsine is condensed in solid form upon the cold dish. This is usually spoken of as Marsh's test for arsenic, and is exceedingly delicate. The merest traces may be detected in this manner. The reaction when the arsine is burning freely in the air is,

$$2AsH_3 + 3O_2 \rightarrow 3H_2O + As_2O_3.$$

The white fumes appearing are the trioxide of arsenic. When a cold dish is held in the flame, this equation shows what is happening,

$$4AsH_3 + 3O_2 \rightarrow 6H_2O + As_4.$$

The hydrogen continues to burn, but the arsenic vapors are condensed in solid form. In making this test precaution must be taken not to light the escaping gas until all the air is removed from the flask. A serious explosion is apt to result if this is not done.

18. **The Oxides.**—There are two oxides of arsenic, the trioxide, $As_2O_3$, and the pentoxide, $As_2O_5$. The first is

much the more common. In commerce it is sold under three other names: arsenious acid, a misnomer, for it is merely the anhydride of arsenious acid, "white arsenic," and "arsenic."

19. **Characteristics of the Trioxide.**—Usually it is obtained as a white powder, although occasionally as a colorless, glass-like solid. Like iodine, carbon dioxide snow, and elementary arsenic it vaporizes without melting. It is slightly soluble in water and forms the corresponding acid, thus,

$$As_2O_3 + 3H_2O \rightarrow 2H_3AsO_3.$$

Taken internally it is a poison, but because of the fact that it is not very soluble it acts slowly. It is used very commonly as a poison for vermin and in large quantities in spraying apple trees to destroy coddling moth. For this purpose it is usually combined with lead acetate to form lead arsenite. This compound is the most desirable because on account of insolubility it is not washed away readily by rains and for the same reason does not "burn" the foliage. Arsenic trioxide is used to some extent in preserving skins in taxidermy and to a limited degree in medicine, especially Fowler's solution, a solution of the trioxide in potassium hydroxide.

20. **Antidotes for Arsenic Poisoning.**—The antidote most generally recommended for arsenic poisoning is freshly prepared ferric hydroxide. It is quickly made by putting together ferric chloride solution and ammonia water, taking care that the ammonia be not present in great excess. A heavy, brownish, flocculent precipitate of ferric hydroxide is formed and this, filtered out, is used in a glass of water. The ferric hydroxide combines with the arsenic forming an insoluble com-

pound which as a result cannot be absorbed by the system. An emetic or stomach pump should follow the antidote. Another sometimes used, which is easier to obtain but slower in action, is magnesium oxide, commonly sold as magnesia. Its chemical action is the same as the ferric hydroxide.

21. **Paris Green.**—This is rather a complicated compound as shown by the formula, $Cu(C_2H_3O_2)_2 + CuHAsO_3$. It will be seen that it consists of copper acetate and acid copper arsenite, combined. Scheele's green is acid copper arsenite, $CuHAsO_3$. Both compounds are bright green pigments and formerly were used extensively in coloring wall papers. Through the probable action of the decomposing paste upon the arsenic compound, volatile compounds were produced which are very poisonous and serious results often followed. Coal tar dyes have now entirely supplanted these pigments for wall papers. Paris green is abundantly used in spraying or dusting potato plants to kill the Colorado beetle. For small patches the powder mixed with flour or air-slaked lime is dusted upon the plants when wet with dew by means of a "shaker," homemade from a baking powder or similar can, by perforating the top with numerous holes. On a large scale the Paris green is usually mixed in water and sprayed on by pumps.

22. **Characteristics of Antimony.**—In the nitrogen family antimony follows arsenic in density with an atomic weight of 120.2. It is a highly-crystallized, lustrous, steel-white metal. Like arsenic it is very brittle, but does not tarnish as readily in the air. It has a melting point of about 445 and upon solidifying it expands greatly. It combines readily with chlorine and bromine, and heated in the air, burns to antimony trioxide.

23. **Uses of.**—In the form of antimony black, a very finely powdered or precipitated antimony, it is often used upon plaster casts to give them a metallic appearance. Its chief use is in alloys. By an alloy is meant an intimate mixture of two or more metals, melted together. They are generally really solutions, although some few are known which seem to partake somewhat of the nature of a compound. The more important alloys of antimony are brittania, pewter, babbitt, stereotype and type metal. The first two are alloys of copper, tin and antimony and are used mainly because they do not tarnish greatly in the air. Babbitt is used for bearings in machinery, as for example those of the crank shaft in motor cars, to reduce friction. Type metal consists of antimony, tin and lead and is of the utmost importance. The antimony causes the expansion of the type metal when it solidifies and thus gives sharp outlines to all the finest details. Made of lead alone, which contracts upon cooling, type would give prints entirely illegible. The purpose of antimony in stereotypes is the same.

24. **Stibine.**—Antimony forms the hydride, $SbH_3$, corresponding to those of the members of this family already studied. It may be prepared as was arsine. It may be liquefied at –18° C. It is even more easily dissociated by heat than is arsine and gives the same spots upon a porcelain dish as does the arsenic, although they are black rather than brown, more soft and velvety in appearance. If heat be applied, since arsenic is volatile, spots made by arsine will disappear, while the antimony will not. Further, a solution of bleaching powder will dissolve the arsenic spots and leave the antimony unaffected.

25. **Antimony Trichloride, $SbCl_3$.**—This compound may be made by dissolving antimony in aqua regia.

It is sometimes called *butter of antimony,* because of the fact if not concentrated to the point of crystallization, it is an oily, yellow liquid, resembling melted butter. In the solid form it is white and crystalline. If water is added, partial solution takes place with the precipitation of a white compound having the formula, SbOCl, antimony oxychloride. The reaction is

$$SbCl_3 + H_2O \rightleftarrows SbOCl + 2HCl.$$

By cautiously adding hydrochloric acid and stirring, the reaction is entirely reversed; upon adding more water the white precipitate again appears. It is an interesting case because it is one of the few in which reversibility is easily seen.

26. **Antimony Trisulphide, $Sb_2S_3$.**—Found in nature this compound is steel-gray, about the color of lead. Prepared in the laboratory by passing a current of hydrogen sulphide through a solution of some antimony compound, it is a beautiful orange colored precipitate which turns dark if melted. It is used extensively in the preparation of matches as previously stated.

27. **Tartar Emetic, $KSbOC_4H_4O_6$.**—From the formula this compound is seen to be basic antimony potassium tartrate. It is one of the few basic salts we have seen. It is a white solid and unlike the chloride is completely soluble in water. It is used somewhat in medicine as an emetic, but like all antimony compounds is very poisonous.

28. **Characteristics of Bismuth.**—Bismuth resembles antimony in general appearance in that it is highly crystalline in structure, but its color is darker and of a purplish or golden luster. It is very brittle, much heavier than antimony with an atomic weight of 208. It melts at about 270° C. With chlorine and bromine its behavior

is about the same as that of antimony. Upon solidifying the metal expands greatly.

29. **Uses.**—While it is eminently suited for type metal on account of its expansibility, being much more expensive, it is rarely thus used, except in delicate stereotypes. One of its most important uses is in making alloys of low fusing point. Some of them are very remarkable in this respect. Thus:

| ALLOY | BISMUTH | LEAD | TIN | CADMIUM | MELT. PT. |
|---|---|---|---|---|---|
| Wood's Metal | 4 parts (270°) | 2 (325°) | 1 (232°) | 1 (320°) | 60.5°C. |
| Rose's Metal | 82 parts | 9 parts | 9 parts | none | 94°C. |

It will be seen that both these alloys melt below the temperature of boiling water, one of them much below. Thus, spoons cast of the former, if placed in a cup of hot tea or coffee would be melted and drop to the bottom. They are interesting illustrations of the fact brought out that solutions have their freezing point lowered. In these alloys bismuth may be regarded as the solvent with a freezing point of 270° C. for freezing point and melting point are the same. When the other metals are dissolved in this, the freezing point is lowered, in one case to 94° and in the other to about 60° C. This low melting property of bismuth alloys enables it to be employed in a variety of interesting ways. Most city ordinances require that the lanterns for moving picture shows be enclosed in a metal or fire-proof booth. The openings are provided with shutters held open by a chain one link of which is made of an easily fusible alloy. In case of the film taking fire this link is easily melted, the shutter closes automatically and the fire is kept within the booth. Metal fire doors, between different apartments in large manufacturing establishments, are often held open during the day by fusible

metal devices. In case of fire, the metal melts and the door is closed by the ordinary air spring attached. Automatic sprinkling systems in large department and wholesale houses employ the same principle. Plugs in the pipes occur at intervals; if fire occurs they are melted and the water is turned on automatically. Steam boilers are likewise often provided with fusible plugs, such as to melt out and allow the escape of the steam before the danger point is reached.

30. **Compounds.**—Not many of these are of sufficient importance to need attention here. The nitrate, $Bi(NO_3)_3$, is a white crystalline solid, prepared by treating bismuth with nitric acid. The reaction is thus shown,

$$Bi + 4HNO_3 \rightarrow Bi(NO_3)_3 + 2H_2O + NO.$$

When water is added a white precipitate forms of the basic or oxynitrate,

$$Bi(NO_3)_3 + H_2O \rightleftarrows BiONO_3 + 2HNO_3.$$

Tested with litmus paper the solution is found to be acidic as is true also when antimony chloride is dissolved in water. The reaction is also equally reversible, as may be shown by the cautious addition of nitric acid. This white precipitate is sold under the name "subnitrate" of bismuth and is used frequently in medicine, as a cosmetic and for stomach trouble. Bismuth forms no compound corresponding to those of arsine and stibine.

31. **Comparison of the Members of the Family.**—Nitrogen and phosphorus in their outward appearance at ordinary temperatures differ greatly from the other three. Nevertheless, nitrogen at low temperatures is a white solid and phosphorus nearly so. In their chemical behavior they are very similar in most respects. As

stated elsewhere, as the elements in a group increase in weight, the tendency, seen best in the oxides, is to become basic or metallic in character. Thus the oxides of nitrogen and phosphorus are strongly acidic; of arsenic, the trioxide has a double character, being both basic and acidic. It reacts with hydrochloric acid to form arsenious chloride, and with sodium hydroxide to form sodium arsenite. The pentoxide, $As_2O_5$, is acidic as might be expected with its higher percentage of oxygen. In the case of antimony, the trioxide is also of dual character, but more strongly basic than acidic, while the pentoxide is still acidic. With bismuth the trioxide is basic only. As further showing this same fact, nitrogen and phosphorus form no salts with these as the positive ions; arsenic forms but few, not very stable, antimony and bismuth many, especially the bismuth. The following table compares the several members in regard to other compounds not already named:

TABLE FOR COMPARISON

| | NITROGEN N = 14 | PHOSPHORUS P = 31 | ARSENIC As = 75 | ANTIMONY Sb = 120 | BISMUTH Bi = 208 |
|---|---|---|---|---|---|
| Hydrogen Compound | Ammonia $NH_3$ | Phosphine $PH_3$ | Arsine $AsH_3$ | Stibine $SbH_3$ | None —— |
| Oxides | $N_2O_3$<br>$N_2O_5$ | $P_2O_3$<br>$P_2O_5$ | $As_2O_3$<br>$As_2O_5$ | $Sb_2O_3$<br>$Sb_2O_5$ | $Bi_2O_3$<br>$Bi_2O_5$ |
| Chlorides | $NCl_3$ | $PCl_3$ | $AsCl_3$(?) | $SbCl_3$ | $BiCl_3$ |
| Oxychlorides | NOCl | POCl | | SbOCl | BiOCl |
| Acids | $HNO_3$<br>—— | $HPO_3$<br>$H_3PO_4$ | ——<br>$H_3AsO_4$ | ——<br>$H_3SbO_4$ | None<br>" |

**Exercises for Review**

1. Name the members of the nitrogen group.

2. From what has phosphorus been mostly prepared? What in very late years? Give a brief outline of the process.

3. Name the forms of phosphorus. Compare them with sulphur. What other elements studied have been seen in allotropic forms?

4. Give the characteristics of yellow phosphorus and compare with it the red.

5. Which is the poisonous variety? What disease do the vapors produce? What remedy is there for it?

6. What is the chief use of phosphorus? Give another use.

7. Give the various steps in the evolution of the common match as we have it to-day.

8. Describe the safety match and state how different from the ordinary.

9. How is phosphine made? What is the chief point of interest regarding it? What use has it?

10. Name the oxides of phosphorus and give formulas. How prepared?

11. Name two or three acids of phosphorus and state how they may be obtained from the oxides.

12. What phosphates occur in nature? Of what use are they? How are they produced artificially for fertilizers?

13. Give the chief characteristics of arsenic.

14. Explain the purpose of the one use of arsenic.

15. How is arsine made? How can you show that it is readily decomposed by heat?

16. What is a nascent gas? How different from the molecular form?

17. Describe Marsh's test in full.

18. Name the oxides of arsenic and give formulas.

19. Describe the trioxide and give uses. What is the antidote for arsenic poisoning? Why may so much time be taken in preparing the antidote?

20. What two pigments of arsenic are common? What former use had they? Why no longer used this way? Chief use now?

21. Give characteristics of antimony and compare with arsenic.

22. What is antimony black? Use of it?

23. Name the most important alloys of antimony and give some use of each? What is an alloy?

24. Give composition of type metal and state wherein is its chief value.

25. How is stibine made? How can its spot be distinguished from that made by arsine?

26. What is butter of antimony? How made? Why so called? When water is added to it, what results? Write the equation.

27. What do you call an equation like the above? How can you prove that it is reversible?

28. How is antimony trisulphide formed in laboratory? Of what practical use is it?

29. Give use of tartar emetic.

30. Describe bismuth and compare with antimony.

31. Give chief uses of bismuth.

32. Name two very fusible alloys of bismuth. Why do they have such a low melting point?

33. Name two compounds of bismuth and state how prepared.

34. Write the equation showing the reaction of water with the nitrate.

35. What kind of an equation is this? How can you show experimentally that it is reversible?

36. Give a general comparison of the members of the group.

37. Show how they become less acidic as they increase in weight.

38. Compare the various oxides of the group in chemical behavior.

# CHAPTER XXIV

## COMPOUNDS OF SILICON

**Outline—**

Natural Compounds—Silica
- (*a*) Variety of
- (*b*) Characteristics
- (*c*) Uses

Artificial Compounds
- (*a*) Water Glass
- (*b*) Crown Glass
- (*c*) Bohemian Glass
- (*d*) Flint Glass

Manufacture of Glass Articles

Annealing Glass

1. **Occurrence of Silicon.**—Silicon belongs to the carbon group. The latter element has already been studied. Two metals, tin and lead, also belong to this group. They all have a valence of four. Next to oxygen, silicon is the most abundant of all the elements and constitutes something more than 25 per cent of the earth's crust. It is never found free as is carbon. In the combined form, sand, $SiO_2$, is a very abundant mineral. Sandstone is the same with some cementing material holding the particles together. Crystallized, this same compound often occurs as hexagonal prisms; when transparent it is then called rock crystal. When delicately colored it is known as rose quartz, amethyst, milky, and smoky quartz, according to the nature of the coloring. Opals, agate, chalcedony, jasper, flint and onyx are other well-known varieties. Much of the agate is petrified wood; as the cells of the woody structure have been broken down in the process of very slow decomposition the sil-

ica has replaced them. The different colors are due to different compounds dissolved in the silica when it was deposited. The most noted of these petrified forests is near Adamana in Arizona. Here trunks of trees of all sizes, for the most part broken squarely across, are found in great numbers, covering many square miles in area. Many of the rocks constituting the crust of the earth are compounds of silicon. Such are kaolin,

Fig. 56.—A scene in one of the petrified forests in Arizona.

feldspar, and the clays resulting from the decomposition of the latter. Mica, which has the property of splitting into thin sheets, commonly used in stoves and often referred to erroneously as isinglass, is a silicate. Granite is ordinarily a mixture of quartz, feldspar and mica. Pumice stone is a porous lava, used as an abrasive and in some washing powders, as "Dutch Cleanser." Infusorial earth, spoken of in connection with the manufacture of dynamite, is a porous, siliceous rock formed

from the shells of microscopic animals. Fig. 56 is a view of a portion of the petrified forests of Arizona.

2. **Characteristics of Silica.**—If pure, silica is colorless. It ranks seventh in the scale of hardness, in which the diamond is tenth. It is not soluble in any acid except hydrofluoric, but is somewhat readily so in alkalies. Some of the hot springs in Yellowstone Park contain very considerable quantities of dissolved silica, so that articles left where the spray may fall upon them, or if dipped into the water repeatedly become covered with a silicious coating. Its melting point is so high that only the electric arc or the oxyhydrogen lamp is sufficient to fuse it.

3. **Uses of Some Forms of Silica.**—The uses of sand for building purposes in mortar and cement are well known. For such work a coarse sand, with grains more or less rough, and not well polished, makes a much stronger wall or foundation. All glass requires sand for its manufacture; sand papers of all degrees of fineness are made for polishing and smoothing wood surfaces. Pure sand is now being made into crucibles and various other chemical apparatus, preferable in many ways to glass. As its coefficient of expansion is very low, it is much less liable to be broken by sudden great changes in temperature. The finer grained infusorial earths are used as abrasives for polishing metals, while sandstone is made into whetstones and grindstones for sharpening tools. The tinted varieties of quartz mentioned are often cut and mounted in cheaper jewelry, where, owing to their hardness, they are very serviceable. Lenses for optical instruments and spectacles are sometimes made from pure quartz.

4. **Silicic Acid.**—Silicon dioxide, $SiO_2$, is an acidic oxide as would be indicated by the fact that it combines

so readily with alkalies. Theoretically, it is the anhydride of silicic acid, but as it is neither soluble in water nor reacts with it, silicic acid is not obtainable by direct means. Orthosilicic acid has the formula $H_4SiO_4$, but when precipitated from a silicate it loses a molecule of water and becomes $H_2SiO_3$. Many salts of these two acids are known.

5. **Water Glass.**—When silica is fused with sodium carbonate, the following reaction takes place,

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2.$$

This sodium salt of silicic acid is generally used in the liquid form, or solution, somewhat resembling glycerine in appearance. If all water is removed, a transparent, colorless solid remains, closely resembling glass. In the viscous solution it is often called "water glass." At the present time very large quantities of it are used. It is probably the best preservative of eggs. For this purpose, a mixture of one part water glass and nine parts of water are put into a jar of suitable size. Into this are put the eggs from day to day, the fresher the better. It is well not to make up a very great quantity of the solution at one time, although there should be sufficient to keep the eggs covered. Any egg which floats in the solution should be discarded as it is already stale and may be the cause of spoiling others. Eggs decompose because of bacteria, which pass through the shell along with the air as it takes the place of the moisture which is being constantly evaporated. The water glass fills and closes the pores of the shell and thus prevents this interchange. Eggs may be thus kept for months and are always far preferable to storage eggs even of less age. The jar and contents must be stored where the contents will not freeze, although a warm room is not desirable.

It may be remembered that the solution will have a freezing point much lower than that of water; hence it will stand a considerable degree of cold. It is well to know that such eggs cannot be boiled without the shells cracking, as a rule. This is because at the boiling point the air contained would be greatly expanded; because it cannot pass through the pores of the shells, it bursts them. After standing for some months a white gelatinous mass will be found collecting in the bottom of the jar. This is silicic acid, and is formed as indicated by the equation,

$$Na_2SiO_3 + 2H_2O \rightarrow H_2SiO_3 + 2NaHO.$$

It has been said that water does not ionize and for that reason is not a conductor of electricity. It does, however, ionize to a *very slight* extent, so that there are always a few hydrogen and a few hydroxyl ions present in the water. Thus,

$$H_2O \rightleftarrows \overset{+}{H} + \overset{- -}{HO}.$$

Sodium silicate, being a salt, is largely ionized, thus,

$$Na_2SiO_3 \rightleftarrows \overset{+}{Na},\overset{+}{Na}, + \overset{- -}{SiO_3}.$$

Therefore, the hydrogen ions colliding with the silicate ions would form silicic acid, and as this is not appreciably soluble in water, it soon begins to separate out as a precipitate. This continues slowly and at the end of some months even an inch or more of white, gelatinous silicic acid may be found at the bottom of the jar. At the same time the hydroxyl ions meeting the sodium ions form sodium hydroxide, but this being very soluble remains largely in the form of ions in the solution. This may be shown by testing with red litmus paper; it is also noticeable in its effect upon the hands, giving the skin a slippery feel-

ing as alkalies all do. Such chemical action as this between a salt and water is called *hydrolysis,* from two Greek words, meaning *decomposition by water.* Various other cases of hydrolysis will be studied later. In reality the action of water upon antimony and bismuth salts, observed in the preceding chapter, is an instance of hydrolysis.

Water glass is also used as a cheap cementing material, in many cases taking the place of glue. This is seen in the manufacture of paper boxes, trunks, and valises.

6. **Crown Glass.**—When lime, sodium carbonate and silica are fused together, a double silicate of calcium and sodium is formed which is called *crown glass.* Unless very pure sand is used there will be small quantities of iron present, which will give the product a green color. It may be largely removed by the addition of some oxidizing material like manganese dioxide; but any slight excess of this compound imparts an amethyst color to the glass. Crown glass has a relatively low melting point; hence, it may easily be softened in the Bunsen burner. It is also more readily attacked by alkalies than some other varieties. However, on account of its cheapness it is used for all ordinary bottles, for common window glass, and most of the test tubes and glass tubing used in the chemical laboratory.

7. **Bohemian Glass.**—When potassium carbonate is fused with sand and lime a variety known as *Bohemian glass* is obtained. It is harder than crown glass, more transparent, less readily attacked by chemical reagents and has a much higher melting point. It is commonly spoken of in the laboratory as "hard glass." It is used for the better chemical glassware—beakers, flasks, and all sorts of other apparatus. The better grades of tumblers

and other glassware in the home are also made from Bohemian glass.

8. **Flint Glass.**—When sand, lead oxide and silica are fused together, a variety called *flint glass* is obtained. In the purest form it is sometimes called *paste*, and from it are made the imitation or paste diamonds. Flint glass is almost perfectly transparent, is very soft so that it is easily scratched, and has high refractive power. Most optical lenses are made from it on account of the ease with which it is cut, its brilliancy and high refractive power. It is the last property that gives the play of colors seen in the imitation diamonds, almost equal to the genuine; but the softness of the glass soon causes a loss of this power. It is also used in the manufacture of cut glass found in the home.

9. **Manufacture of Glass Articles.**—Tumblers and similar articles of household use are molded. A sufficient amount of molten glass is put into a heated mold the size

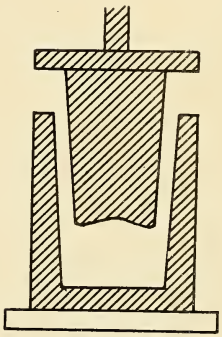


Fig. 57.—Mold for making glass tumblers.

and shape of a tumbler. As shown in Fig 57, a rod descends, mechanically, bearing a solid but smaller tumbler. This squeezes the molten glass into the space

between the two and in a second of time the glass is done. Bottles are made by blowing. A suitable amount of molten glass is taken from the furnace upon the end of a blowpipe. (See Fig. 58.) This is placed within a mold, and by lung power or compressed air the glass is blown until it issues from the top of the mold in the form of a

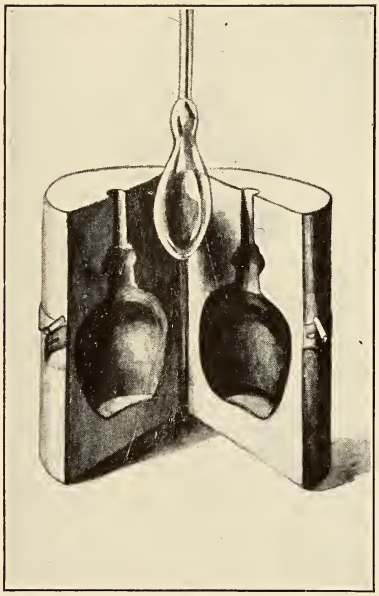


Fig. 58.—Mold for blowing glass bottles. The blow-pipe with molten glass is shown hanging within the opened mold.

large bubble and bursts. Immediately, the bottle with its ragged top in placed in another machine which, while the glass is still soft, turns it round and round until the neck and top are perfectly smooth. Ordinary window glass is first blown into long cylinders. These are cut lengthwise and flattened out while still hot, just as a

roll of paper might be with a pair of scissors. (See Fig. 59.) Heavy plate glass is made by pouring a ladle of molten glass upon a table and immediately rolling until it covers the top of the table and has attained a uniform thickness. It is then polished by revolving discs with water and pumice or some similar abrasive. The color of

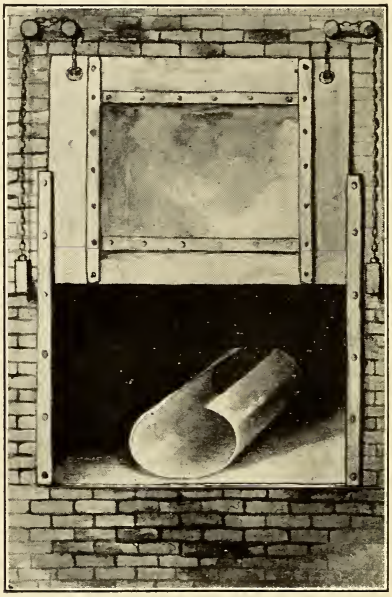


Fig. 59.—Making window glass. It is first blown into form of a cylinder. This is cut open, flattened out and annealed.

glass articles is secured by the introduction of small quantities of some other compound. It has already been stated that manganese gives an amethyst color; cobalt gives a beautiful, deep blue; copper a lighter or greenish blue; chromium a clear, beautiful green; calcium fluoride a translucent white; iron, pale green, yellow or brown,

according to the kind of iron salt introduced; gold and some copper compounds give a red color.

A glass rod kept soft by heat may be drawn out into thread and wound like silk fibers upon a large wheel or bobbin. From this it may be woven into various articles such as ribbons, bows for neckwear and even into cloth. Thus used it has the sheen of satin, but naturally it is not very durable.

10. **Annealing Glass.**—All glass articles when first made are very brittle. Annealing consists in cooling them so very slowly that the molecules are enabled to move into relatively stable positions. This is done by putting the articles into a very long oven, one end of which is extremely hot. They are then very slowly moved mechanically toward the cooler end and after several days are ready for packing and shipping.

### Exercises for Review

1. What can you say of the abundance of silicon compounds in nature?

2. Name several varieties of quartz.

3. Name several other minerals consisting of silica, some of which are prized for their beauty.

4. What is petrified wood? How formed?

5. Give the characteristics of quartz.

6. Mention some uses for some of the natural forms of silica.

7. What kind of an oxide is silica? What acid is formed theoretically from it?

8. How is water glass made? In what form is it used?

9. Give method of preserving eggs with water glass.

10. Why do preserved eggs crack when boiled?

11. What is meant by hydrolysis? Illustrate by means of sodium silicate.

12. Name two cases of hydrolysis in a preceding chapter.

13. How is crown glass made? Give some common uses for it. Why is it green in color? How may this be removed?

14. From what is Bohemian glass made? Give its differences from crown.

15. What laboratory uses have these two kinds of glass, and why?

16. From what is flint glass made? Give its most important uses. Why so used? What use has it in our homes?

17. Give the common method of making tumblers. How are bottles made? Plate glass? Window glass?

18. What is meant by annealing? How is it done? What is really accomplished by annealing?

# CHAPTER XXV

## THE ALKALI METALS

**Outline—**

Comparison of the Members
Sodium
(*a*) Occurrence
(*b*) Method of Preparing
(*c*) Characteristics
(*d*) Uses
Compounds
(*a*) Sodium Chloride
(*b*) Sodium Bicarbonate
(*c*) Sodium Carbonate
(*d*) Sodium Hydroxide
(*e*) Soap
(*f*) Borax
(*g*) Hydrolysis of Compounds
Potassium
(*a*) Occurrence
(*b*) Characteristics
Compounds
(*a*) Potassium Carbonate
(*b*) Potassium Hydroxide
(*c*) Potassium Nitrate
(*d*) Potassium Chlorate
(*e*) Other Compounds

1. **General Comparison.**—This group includes the most strongly positive metals, as the halogen group does the most strongly negative. They occupy a position at the left end of the periodic table while the halogens are at the extreme right. The two important members are sodium and potassium; the other three, lithium, cæsium and rubidium, are much less common. More or less vigorously they all decompose water, forming strong

bases or alkalies, for which reason they are commonly called the *alkali metals.*

2. **Occurrence of Sodium.**—Common salt is one of the most familiar of all substances. It occurs in small quantities in nearly all soils; it is present in the dust particles floating in the air; it is the sodium in this compound which colors a flame yellow when a room is being swept. A clean platinum wire, drawn through the fingers, in a Bunsen flame will give the characteristic yellow coloration. It is found in the blood to the extent of 0.8 per cent. About seven-tenths of the solid matter found in sea water, or nearly 3 per cent by weight, is common salt, and amounts to the astonishing sum of over 35,000 billion tons. Some one has calculated that on the basis of an average depth of 1,000 feet, the common salt in the various oceans would occupy a bulk of 3,500,000 cubic miles and that if this were separated out and piled up it would make a mountain range rivaling in height and length some of our great western chains. In some of the Middle-West States, notably, Kansas, deposits of nearly pure salt are known, 300 feet in thickness, covering vast areas. Likewise, New York, Ohio and Michigan have extensive deposits and these three states together with Kansas furnish about nine-tenths of all the salt made in the United States. California, Utah, West Virginia, Pennsylvania, Louisiana, Texas and Oklahoma also produce considerable amounts. In California one or more lakes covering an area of from 30 to 50 square miles are known, saturated with salt: a crust 6 to 8 inches in thickness of nearly pure salt covers the surface over which in the dry season anyone may walk with safety. These lakes glisten in the sun like one in our northern climates, frozen over and covered with snow. Chile saltpeter, $NaNO_3$, is another abundant natural

compound but not so widely distributed as common salt. It is found mostly in the desert areas of Chile, covering about 450 square miles or about the size of a single county in some of the Middle-West states. The deposits are from 25 to 50 per cent sodium nitrate and something like 5 feet in thickness, while the quantity is considerable it is far from unlimited. Other natural compounds of sodium are known, but they are unimportant.

3. **Preparation of Sodium.**—Sir Humphrey Davy, in 1807, first prepared the metal by the electrolysis of sodium hydroxide. At the present time the same method is used, improved, and known as the Castner process. Fig. 60 gives an idea of the apparatus. The sodium hydroxide is melted in a vessel, marked V, usually made of cast iron; to this is attached the cathode in the form of a bundle of carbon rods. The anode, marked W, is a vessel, similar to V, inverted over and dipping into the melted caustic soda. In the center, the vessel, P, which reaches down below the upper end of the carbon rods is the receiver for the sodium and is closed at the bottom by a coarse wire gauze. The current causes the sodium and hydrogen, both positive, to collect upon the carbon rods, from which they rise to the top within the vessel, P. The hydrogen escapes and the sodium when cooled is removed and molded into sticks. The

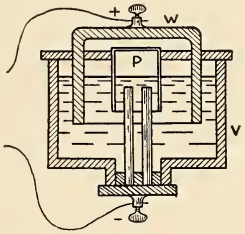



Fig. 60.—Preparation of sodium by the Castner process.

oxygen collects upon the vessel, W, which is the anode, from which it may be drawn off or allowed to bubble out and escape.

4. **Characteristics.**—Sodium is a silvery-white metal, at ordinary temperatures soft and pliable. It reacts vigorously with water and must be kept under naphtha or some hydrocarbon oil free from oxygen. Exposed to the air it rapidly attracts the moisture, with which it reacts and forms sodium hydroxide. This in turn absorbs the carbon dioxide and forms sodium carbonate, so that ultimately the metal when exposed to the air becomes a white, brittle mass. On a vessel of water at room temperature a piece of sodium rolls about, gradually diminishing in size, until it finally disappears. On warm or hot water the heat generated is sufficient to ignite the hydrogen evolved and volatilize small portions of the sodium which color the flame yellow. On wet blotting paper, a small bit of sodium, not able to roll around, soon becomes hot enough to melt, at a temperature but little below the boiling point of water, 96° C. It is then a silvery globule like mercury; if dropped upon the floor at this point it breaks into numerous smaller globules which burn with the usual yellow flame as they roll off in all directions. The irritating white fumes which arise as the metal thus burns are sodium peroxide, $Na_2O_2$. Sodium is soluble in mercury, and if present in sufficient quantity forms a solid *amalgam*, an alloy of which one constituent is mercury. This readily decomposes water, but less rapidly than sodium alone. The fact is made use of in the electrolytic process of making chlorine described on p. 122. Sodium may be converted into vapor at about 750° C. The density of the vapor shows it to be monatomic. When heated sodium combines readily with both oxygen and chlorine; the oxy-

gen compound thus obtained is the peroxide, spoken of elsewhere as "oxone" used in preparing oxygen.

5. **Uses.**—Sodium has no commercial uses. In drying some organic compounds and in some other laboratory work it is of value. The preparation of artificial rubber, still in the experimental stage, employs sodium in one step of the process.

6. **Compounds.**—The occurrence of sodium chloride in nature has already been mentioned. It is obtained from these sources in two or three ways. A very considerable amount is mined as any other mineral. Since more or less insoluble foreign matter usually accompanies this rock salt as it is called, it is largely used for stock, or crushed to coarse grains for making freezing mixtures for refrigeration and for keeping ices and creams. At Salt Lake, Utah, the water, already saturated, is pumped into basins and evaporated by the heat of the sun. The product is somewhat impure but suitable for refrigeration and for packing purposes. At San Francisco the water is pumped likewise into basins and evaporated. Most of the salt used upon the table and in food products is obtained from salt wells. These are drilled down to reach the layer of salt, water is run in and allowed to remain until saturated. It is then pumped out and after any insoluble matter has settled out, it is evaporated and crystallized.

7. **Characteristics of Salt.**—Salt obtained from wells is comparatively pure. Usually it contains a very small percentage of magnesium chloride which, being deliquescent, causes the whole mass to become damp in wet weather. If a stream of hydrogen chloride be passed through a saturated solution of salt, pure sodium chloride will separate out in fine crystals. As the magnesium chloride contained is usually less than $\frac{1}{2}$ of

1 per cent and most of the samples of salt upon the market assay from 97 to 99 per cent in purity, it is not necessary, except for some chemical purposes, to purify the commercial supply. At the present time several brands of table salt may be obtained which do not cake in damp weather. They have not been freed from the magnesium chloride, but have had some finely powdered substance like starch or cooking soda or prepared chalk in very small amounts intimately mixed with the salt,

Fig. 61.—Preparation of salt in San Francisco Bay, by evaporation of sea water.

so that the individual grains are protected from the air by a thin coating of the powder. It will probably be found, if the label upon the container is read, that the adulterant used will be stated. As the substance thus employed is harmless and always in very small proportions, it cannot be said to be especially objectionable. Upon the lower organisms salt is altogether destructive. Such is the explanation of its preservative qualities. Sprinkled upon such soft bodied animals as snails and

slugs, which in some parts of our country grow to great size, salt seems to extract the moisture from the body. It shrinks rapidly in size, and the animal soon dies. In large amounts it is harmful to the human body, and in some countries has been frequently used as a means of suicide. In small quantities it is regarded not only as not harmful but even necessary for the body, to provide the hydrochloric acid needed in digestion. Undoubtedly, however, nearly everyone uses much more than necessary, so that it must be eliminated by the skin in the perspiration and through other excretory organs.

8. **Uses.**—It is said that about 11 pounds per capita of refined salt is used every year in the United States in the seasoning of foods. Much more is employed in the preservation of meats and meat products. Altogether, statistics show that the total quantity used every year in various ways amounts to 30,000,000 barrels, more than a barrel for every family of four individuals. Besides these uses, so familiar to all, salt forms the starting point in the manufacture of several very important compounds which will be studied later.

9. **Sodium Bicarbonate.**—This compound, chemically known as acid sodium carbonate with formula $NaHCO_3$, is common cooking soda. The word *bicarbonate* means *twice carbonated,* and was so given because the compound was formerly prepared by passing a stream of carbon dioxide into a solution of sodium carbonate, whereupon the bicarbonate, being much less soluble, crystallized out. Thus it was obtained by carbonating sodium carbonate. The equation shows the reaction,

$$CO_2 + Na_2CO_3 + H_2O \rightarrow 2NaHCO_3.$$

At the present time the commercial supply is made by what is known as the Solvay process. A saturated solu-

tion of salt is treated with ammonia and carbon dioxide when three reactions take place, thus,

$$NH_3 + H_2O \rightarrow NH_4HO,$$
$$NH_4HO + CO_2 \rightarrow NH_4HCO_3,$$
$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl.$$

As the acid carbonate is not very soluble in water it crystallizes, after which it is removed, dried and pulverized, usually, for the commercial supply. The ammonium chloride solution is saved, treated with lime and heated, whereupon the ammonia is recovered to be used again in the first step of the process. It will be seen, therefore, that the manufacture is very cheap,

$$2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O.$$

10. **Sodium Carbonate.**—The greater portion of the acid carbonate made by the Solvay process is converted into the normal carbonate by heating, thus,

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

The carbon dioxide thus obtained is used in the first step of the process described above for making sodium bicarbonate, which still further cheapens the process. Another method, known as the Leblanc process, was used for many years. This consisted in the conversion of common salt into sodium sulphate by strongly heating with sulphuric acid during which reaction hydrogen chloride was evolved. (See p. 126.) By further treatment of the sodium sulphate thus obtained with coke and limestone the sulphate was converted into a carbonate which was separated from the mixture by dissolving in water. The process is much more complicated and expensive than the Solvay and would now be abandoned were it not for the by-product obtained, hydrochloric acid. By the Solvay process *anhydrous* sodium carbonate

is obtained; by the Leblanc, the hydrate, $Na_2CO_3 \cdot 10H_2O$. This is known as *sal soda* or *washing soda*. It is strongly efflorescent and when exposed to the air rapidly loses nine of the water molecules contained. Heat is necessary to remove the remainder. Sodium carbonate is a neutral salt, yet, dissolved in water, it gives an alkaline reaction with litmus. This is explained in the same way as in the case of the water glass, p. 298. The sodium carbonate in water is largely ionized, thus,

$$Na_2CO_3 \rightleftarrows \overset{+}{Na},\ \overset{+}{Na} + \overset{--}{CO_3}.$$

Water forms some few ions,

$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{HO}.$$

The hydrogen ions reacting with the carbonate ions produce carbonic acid. This, however, is an exceedingly weak acid, and, as is true of all weak acids, is *very slightly* ionized, hence exists almost entirely in the molecular form. The hydroxide ions reacting with the sodium form sodium hydroxide, which being a very strong base is largely ionized. Thus a very considerable amount of hydroxide ion is always present in such a solution. As the alkali reaction is due to the presence of hydroxide ions a solution of sodium carbonate always turns litmus paper blue.

11. **Further Study of Hydrolysis.**—As stated above the alkaline reaction of sodium carbonate is due to hydrolysis. It is of such importance as to merit further study. Common salt dissolved in water shows no litmus reaction. The reason may be seen by writing the ionic reactions,

$$NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl}$$

$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{HO},$$

When the ions present react, two new products form, NaHO and HCl. As one is a strong base and the other a strong acid they give relatively equal quantities of hydrogen and hydroxide ion and hence neutralize each other so that there is no litmus reaction. If sodium sulphate be used, like results are obtained,

$$Na_2SO_4 \rightleftarrows \overset{+}{Na},\ \overset{+}{Na} + \overset{--}{SO_4},$$
$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{HO}.$$

The new products are sulphuric acid and sodium hydroxide, both strong. Again the hydrogen ions and hydroxide ions practically neutralize each other and there is no litmus reaction. This is true of all salts formed by the union of a strong base and a strong acid. It is usually stated thus: *Salts formed by the union of a strong base uniting with a strong acid are not hydrolyzed appreciably in water.*

Salts like sodium carbonate and sodium silicate are the result of the union of a strong base and a weak acid and give alkaline reaction. Conversely, salts formed from a weak base and a strong acid give an acid reaction. This will be evident if the ionic equations are written,

$$FeCl_3 \rightleftarrows \overset{+++}{Fe}, + \overset{-}{Cl},\ \overset{-}{Cl},\ \overset{-}{Cl},$$
$$H_2O \rightleftarrows \overset{+}{H} - \overset{-}{HO}.$$

The new products formed are hydrochloric acid and ferric hydroxide. The acid is very strong, while the base is weak; obviously, therefore, the litmus reaction will be acid in character.

$$CuSO_4 \rightleftarrows \overset{++}{Cu} + \overset{--}{SO_4}.$$
$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{HO}.$$

In the above solution the base formed will be copper hy-

droxide which is weak and the acid sulphuric which is strong. Again the litmus reaction will be acid. All such salts behave in a similar manner. This case is usually expressed thus: *Salts formed by the union of a weak base with a strong acid, or conversely, by the union of a strong base with a weak acid are partially hydrolyzed.* They give an acid or alkaline reaction according as the acid or the base is the strong factor.

There is a third class of salts formed by the union of a weak base with a weak acid. Such are ferric carbonate and aluminum sulphide. Ionically written, ferric carbonate gives

$$Fe_2(CO_3)_3 \rightleftarrows \overset{+++}{Fe},\ \overset{+++}{Fe} + \overset{--}{CO_3} + \overset{--}{CO_3} + \overset{--}{CO_3},$$

$$H_2 \rightleftarrows \overset{+}{H} + \overset{-}{HO}.$$

The ferric ions collide with the hydroxide ions and give ferric hydroxide; likewise, the hydrogen and carbonate ions form carbonic acid. Both compounds are ionized very slightly. The result is the molecules accumulate; the solution becomes saturated with carbonic acid and at once it begins to decompose with the escape of carbon dioxide, thus,

$$H_2CO_3 \rightarrow H_2O + CO_2.$$

Thus the carbonate ions are constantly forming molecules of carbonic acid and this is being destroyed by the escape of the carbon dioxide, so that it is removed from the sphere of action. Likewise, the ferric hydroxide, not being appreciably soluble in water, begins to form a precipitate and it also is removed from the sphere of reaction. The ultimate result is that practically all the carbon dioxide escapes and the ferric ions have formed ferric hydroxide which alone remains as a precipitate. In other words, ferric carbonate in water has been converted entirely into ferric hydroxide, that is completely decom-

posed. The conclusion is usually stated thus: *Compounds formed by the union of a weak base with a weak acid in water are completely hydrolyzed.* The action of one class of baking powders depends upon this very fact and will be taken up at another time.

12. **Uses of Sodium Carbonate.**—Its chief use is for the manufacture of other compounds. With silica it is used in making two varieties of glass; it is also used in preparing sodium hydroxide, a very important compound to be studied later. It is used extensively in softening water and is the chief constituent of most washing powders. In addition, these may contain powdered caustic soda, borax, pumice stone, soap powder, sodium peroxide, and possibly sometimes some other substances. Scouring powders usually contain pumice; if put into a glass of water and stirred the other ingredients will dissolve leaving the pumice as a gray deposit. "Dutch Cleanser" is a washing powder of this kind. They are excellent in their way, but should not be used on highly polished surfaces such as silverware and the like.

13. **Sodium Hydroxide.**—This compound, NaHO, is commonly called caustic soda. In an impure form it is frequently sold at groceries under the name of "lye." Much of it is prepared from sodium carbonate by treating it with slaked lime thus,

$$Ca(HO)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHO.$$

The calcium carbonate is not soluble in water, hence forms a precipitate from which the caustic may be drained off. A considerable amount of sodium hydroxide is also made electrolytically as described under chlorine. Made thus it is much more apt to be pure than by the other process; in fact, commercial caustic

soda made from sodium carbonate often contains as much as 25 per cent of the latter compound or other impurities. For most of its uses such impurities, however, are not especially objectionable. To obtain pure caustic soda from this commercial variety it is dissolved in alcohol, filtered and the solvent evaporated. The impurities do not dissolve in the alcohol, hence are left behind in the filtration.

14. **Characteristics of Sodium Hydroxide.**—It is a white solid: the pure caustic is usually sold in the form of small sticks although it may be had in a powder. The commercial variety is usually powdered. It is exceedingly caustic when moist, and is very deliquescent. Exposed to the air it rapidly dissolves in the moisture present, takes up carbon dioxide, and ultimately, as stated in the case of sodium, forms solid sodium carbonate.

15. **Uses.**—As already stated caustic soda is a constituent of many washing powders. It is used in the manufacture of paper pulp, in decomposing the woody fiber; also in many other manufacturing processes. Probably its most extensive use is in the manufacture of soap.

16. **Soap.**—Soap is a salt which in water gives an alkaline reaction because of hydrolysis. It is prepared by treating some fat or oil with caustic soda. The reaction is shown by the following equation,

$$3NaHO + C_3H_5(C_{17}H_{35}COO)_3 \rightarrow 3NaC_{17}H_{35}COO + C_3H_5(HO)_3.$$

Stearin has been used here as typical of the other fats. It will be noted that glycerine is the by-product. On a large scale, soaps are generally made from the waste fats, or those of animals condemned by inspectors at

the packing houses as unfit for food, and from other similar sources; also from some of the cheaper oils. The yellow rosin soaps usually contain considerable rosin substituted for a portion of the fat. The chemical process in the making of soap is called *saponification*. Chemical reaction with organic compounds is nearly always slow, for the reason that they are not ionized. Hence, three or four days of constant boiling are necessary for the completion of the process. At the end of this time, salt is added, which causes a more perfect separation of the salt and glycerine. The salt water with the glycerine is drawn off beneath the soap layer, evaporated until of such concentration that the salt will crystallize out, after which the glycerine is concentrated in "vacuum pans" under partial air pressure. If potassium hydroxide is used instead of sodium, a soft soap is obtained in which the glycerine remains dissolved. In small quantities it is prepared for use in pharmacy, from pure fats or oils, especially linseed. Formerly, practically all the soap used by those living in the country was home-made. The ashes obtained during the winter months were put into hoppers and kept dry. In the spring lime was added and the mixture leached with water, added in small quantities at a time. These reactions took place,

$$CaO + H_2O \rightarrow Ca(HO)_2,$$
$$Ca(HO)_2 + K_2CO_3 \rightarrow CaCO_3 + 2KHO.$$

The water, which slowly trickled from the hopper, contained the potassium hydroxide and was called lye. It was then boiled in large iron kettles with any waste fats that had accumulated during the winter. If hard soap was desired, when saponification was complete, salt was added and the whole allowed to cool. The soap floated on the spent lye and when cold could be lifted off and cut

into cakes. Made thus it is always brown in color and usually contains more or less free alkali. Since soap is a salt made by the union of a strong base and a weak acid, in water owing to hydrolysis, it will give an alkaline reaction even if there be no free alkali contained. To determine whether the sample be devoid of free alkali, some of it must be dissolved in alcohol which does not cause hydrolysis. A strong alkaline test in such a solution indicates free alkali in the soap. Floating soaps are produced partly by forcing minute bubbles of air into the soap before it is made into cakes and partly by the removal of much of the water present. They are more durable than soaps containing much water, although possibly a little slower in producing a "suds" or lather. Transparent, glycerine soaps are made by dissolving ordinary soap in alcohol and filtering out the insoluble residue; the alcohol is recovered by distillation. Such soaps are expensive because of the added labor in preparing them and also from the fact that they dissolve rapidly in water and hence do not last well. Many soaps contain fillers, that is substances like sodium carbonate or water glass worked in by "crutchers." These consist of a large endless screw like an augur fitting somewhat loosely within a large upright cylinder. The warm, pasty soap is run into these, the filler added and the screw started. In the course of several hours the whole is thoroughly mixed. Some of these fillers, especially sodium carbonate, are not particularly objectionable, but the value of the water glass is doubtful. All of them cheapen the cost of the soap to the manufacturer. From the crutchers the soap is run into large molds holding several hundred pounds, where it hardens. It is removed from these, allowed to dry several weeks, is then cut into bars, pressed

into cakes by machinery, wrapped and packed almost entirely without the touch of a human hand.

17. **Sodium Nitrate, $NaNO_3$.**—This compound is known commercially as Chile saltpeter, and has been mentioned elsewhere. It is a white, crystalline solid, used for the manufacture of gunpowder, nitric acid and extensively as a fertilizer.

18. **Borax.**—Chemically, borax is sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$. Our supply is obtained principally from the deposits of calcium borate in California. This natural compound is treated with sodium carbonate with the following reaction,

$$CaB_4O_7 + Na_2CO_3 \rightarrow CaCO_3 + Na_2B_4O_7.$$

The mixture is treated with hot water which dissolves out the borax, but not the calcium carbonate. When crystallizing the salt takes up ten molecules of water. It is a white solid, somewhat efflorescent, giving an alkaline reaction in water due to partial hydrolysis. It is used in many washing powders, but is more expensive than sal soda. Small quantities are used in the chemical laboratory in testing for various metals. When fused in a loop on the end of a platinum wire, it loses its water of combination and forms a perfectly transparent glass; now, if this is dipped into a solution of certain metals and again fused, or if a minute portion of certain oxides be fused with it, it forms beautifully colored "beads" which are distinctive. For example, cobalt gives a deep blue; nickel a brown; chromium a bright emerald green; manganese, amethyst. It is commonly used in hard soldering as a flux. There is always a film of oxide more or less thin upon the surface of nearly every metal. If solder is poured upon such a surface it will not adhere because it does not really come in contact with the

metal. When borax is applied, it melts, at the temperature necessary for doing the work, dissolves the thin film of oxide, and leaves a perfectly clean metal to which the solder strongly adheres.

19. **Occurrence of Potassium.**—The third member of the sodium group in point of density is potassium with an atomic weight of 39. It is found in several natural compounds, but much less abundantly than sodium. The most common is potassium chloride, mixed usually with magnesium chloride. Most salt lakes contain small quantities of both potassium and magnesium chloride. The presence of magnesium chloride in table salt has already been mentioned. As these two chlorides are much more soluble in water than common salt, they will remain in solution until most of the sodium chloride has already crystallized out. Thus, in the famous Stassfurt deposits of Germany, the lower portions, many hundreds of feet in thickness, are common salt, while the upper layers contain much potassium and magnesium chloride. Probably the same will be found true when the Great Salt Lake in Utah and other similar lakes in this country have finally become dry. At present, the portion separating out is largely sodium chloride, while the water still contains the greater part of the magnesium and potassium compounds. Potassium nitrate is also found in nature, but not in such quantities as the sodium nitrate beds of Chile.

20. **Preparation of Potassium.**—Potassium was first prepared by Davy by the same method he used for making sodium, and in the same year. Later, for many years the commercial supply was obtained by heating potassium hydroxide with carbon. Now, however, it is made electrolytically by a process similar to that of sodium.

21. **Characteristics of.**—Potassium is a silvery-white metal, lighter than water, with a melting point of about 63. Small quantities of the metal volatilized in the Bunsen flame give a violet color. This generally serves as the test for potassium salts, just as the yellow flame does for sodium. The vapor of potassium is green in color. The density of the vapor shows that it is monatomic. It reacts vigorously with water even if cold, with the evolution of sufficient heat to ignite the hydrogen set free. Sufficient of the metal is always at the same time volatilized to color the flame decidedly violet. The following equation shows the reaction,

$$2K + 2H_2O \rightarrow H_2 + 2KHO.$$

Exposed to the air reactions similar to those in the case of the sodium occur with the ultimate formation of potassium carbonate. It must, therefore, like sodium, be preserved in some oil like naphtha which contains no oxygen. Outside the chemical laboratory potassium has little use.

22. **Potassium Carbonate, $K_2CO_3$.**—Years ago considerable quantities of this salt were obtained from wood ashes. From their treatment in large iron pots, the salt extracted by the water came to be known as *potashes,* and later as *potash,* from which the name of the metal was derived. Since the disappearance of many of the original great forests, this source has become negligible. At the present time, sugar beets furnish a very considerable amount. The sap is boiled down in vacuum pans to the point at which the crystallizable sugar will separate out; the portion which will not crystallize is known as molasses and is separated from the sugar by centrifugal machines. The molasses is fermented with yeast and made into alcohol. From the residue the potas-

sium carbonate is obtained. Another source of considerable potassium carbonate is the wool of sheep. An oily substance called *suint* which sometimes equals the weight of the clean wool itself is secreted by the glands of the skin. This is removed from the wool by hot water; from it potassium carbonate and a valuable oil are obtained. Some potassium carbonate is also prepared from potassium chloride, as sodium carbonate is made from the chloride. Potassium carbonate is a white crystalline salt, which is very deliquescent. Commercially, it is known as *pearl ash*. As already stated, it is used in making Bohemian and flint glass. From it also potassium hydroxide is prepared.

23. **Potassium Hydroxide, KHO.**—This is made by processes exactly similar to those for making sodium hydroxide, thus,

$$K_2CO_3 + Ca(HO)_2 \rightarrow 2KHO + CaCO_3.$$

The calcium carbonate is an insoluble compound and the hydroxide may be decanted or filtered off. It may also be prepared electrolytically from potassium chloride as is caustic soda. Commercially it is known as caustic potash. It is a white solid, extremely deliquescent, and caustic, similar in all respects to caustic soda. It is used chiefly in making soft soap; a special variety prepared for the drug trade is made by combining the caustic potash with linseed oil. This is used in making certain salves and other pharmaceutic preparations.

24. **Potassium Nitrate, $KNO_3$.**—This compound occurs in limited quantities in the soil in certain parts of Persia and India. It is supposed to be formed through the action of bacteria upon animal refuse. Considerable amounts are made from Chile saltpeter by treating that salt with potassium chloride. Potassium nitrate is a

white crystalline salt, not greatly different from common salt in taste. Commercially, it is known as *saltpeter*. It is used to some extent in curing meats but mainly for making gunpowder. The composition is not materially different from that given when sodium nitrate is used, 75 per cent of the mixture being saltpeter. Sulphur and charcoal with a little moisture make up the balance. When exploded, the gases formed are mostly nitrogen and one or both of the oxides of carbon. The smoke produced when fired in a gun is a mixture of two or more solid compounds, mainly potassium sulphide and potassium carbonate. Partly because of the smoke and partly because less powerful, ordinary black powder is being largely supplanted by smokeless powders which have been mentioned on p. 156.

25. **Potassium Chlorate, $KClO_3$.**—This salt is a white crystalline solid. It melts easily in the Bunsen burner and decomposes, forming potassium chloride. All the oxygen is evolved, thus,

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

In the presence of manganese dioxide, which serves as a catalytic agent, when heated the decomposition is rapid. Potassium chlorate is used in the preparation of oxygen, in making fireworks, and in matches, as already described. It has a mild, cooling taste, and is sometimes used to allay irritation of the throat and coughing.

26. **Other Compounds.**—Potassium bromide and iodide are white compounds which crystallize in cubes considerably larger than those of common salt. They are both very soluble in water, and are both used to some extent in medicine. The former is a sedative and the latter an alterative. Potassium bromide is also used in photography as a means of preparing the silver bromide

upon the plates and films. Potassium cyanide, KCN, is a white compound, very deliquescent, with a peculiar, unpleasant odor. It is one of the most violent poisons known. Its chief use is in silver and gold plating and as a means of extracting gold from its ores by what is known as the cyanide process.

### Exercises for Review

1. Name the metals of the sodium group. By what other name are they known? Why so called?

2. Give in some detail the occurrence of common salt upon the earth.

3. Who discovered sodium? How is it prepared now?

4. Describe sodium. How is it preserved? Why?

5. What is an amalgam? What use is made of sodium amalgam?

6. Give methods of preparing common salt for the market.

7. Give the chief properties of common salt.

8. What causes table salt to become damp? How is this prevented in some samples?

9. Give uses for common salt. State amount used per capita.

10. What is sodium bicarbonate? How did it receive the name? How is it prepared now?

11. How is sodium carbonate made? Give steps in the Leblanc process and write the equations, omitting the coke from your last equation.

12. Give some important uses for sodium carbonate.

13. What is sal soda? Why does it give an alkaline reaction in water?

14. What is hydrolysis? State what kind of a litmus reaction a solution of each of the following will give: sodium nitrate, potassium sulphate, copper chloride, potassium carbonate, aluminum sulphate, potassium chloride, ammonium nitrate.

15. Describe the reason for each case of the above.

16. Describe caustic soda and give uses.

17. How is soap made? What by-product is obtained? How is it separated?

18. How can you determine whether a soap contains free alkali? Why will all soaps dissolved in water give an alkali test?

19. Give the chemical names for borax, caustic soda, Chili saltpeter, pearl ash, baking soda, sal soda, caustic potash, saltpeter.

20. Give some uses for borax. Explain what it does as a flux in soldering.

21. Describe potassium and compare with sodium.

22. What is the origin of the word potassium? Give three sources of potassium carbonate. What uses has it?

23. What is saltpeter used for? What is produced when gunpowder is exploded?

24. Why are smokeless powders supplanting ordinary black powder?

25. Describe potassium chlorate and give uses. What is its purpose in a match head?

26. What use has potassium cyanide?

27. Give formulas for sal soda, anhydrous sodium carbonate, potassium chlorate, borax, caustic soda, pearl ash.

28. Complete the following equations and state what they indicate:

$Na_2CO_3 + Ca(HO)_2 \rightarrow$ ,
$KClO_3$ heated $\rightarrow$ ,
$Na + H_2O \rightarrow$ ,
$H_2SO_4 + NaCl \rightarrow$ ,
$NaHCO_3$ (heated) $\rightarrow$ ,
$K_2CO_3 + H_2O \rightarrow$ .

*Note.*—In completing these equations, the student may use any quantity needed.

# CHAPTER XXVI

## SOME LEAVENING AGENTS

**Outline—**

Chemical Agents
- (*a*) Baking Soda
- (*b*) Baking Powders
- (*c*) Comparative Healthfulness

Yeast as a Leavening Agent
Salt-rising Bread
Aerated Bread
Beaten Biscuits

1. **Baking Soda.**—The most common chemical reagent used in leavening bread is sodium bicarbonate, sold as *soda* or *baking soda.* It has been in use for years. The flour with the soda well-mixed is "wet up" with sour milk or buttermilk both of which contain lactic acid. The acid reacting with the soda, forms carbon dioxide as shown by the following equation,

$$NaHCO_3 + HC_3H_5O_3 \rightarrow CO_2 + H_2O + NaC_3H_5O_3.$$

The carbon dioxide, formed throughout the dough, when greatly expanded by the heat of the oven, tends to escape. In most flours there is a considerable amount of a compound called "gluten" through which the gas cannot readily pass: in its effort, however, the dough is raised and the bread is made light and porous. This gluten may be obtained for examination by tying a spoonful of flour in a thin cloth and washing for sometime in cold water. The starch granules will pass through the cloth and disappear in the water. A sticky, gummy mass, which is mainly gluten, will be left behind. It is a nitrogenous compound and is the muscle building part of the flour.

There is one difficulty in the way of successful use of soda as a leavening agent. It has been explained elsewhere, that it is the lactose, or milk sugar, that by fermentation produces the lactic acid in sour milk. When the milk first begins to taste sour the quantity of acid present is not large, but continually increases until all the lactose has been changed. It is impossible to know without chemical test how much soda is needed to neutralize the acid present. Hence, too little may result in a sour and heavy bread, or too much may produce a discolored, alkaline-tasting bread. In very warm weather the decomposition of milk is rapid: as it is an excellent medium of growth for all kinds of bacteria other products besides lactic acid form, which may result in an unwholesome bread.

2. **Baking Powders.**—The uncertainty of the results to be expected from the use of soda with sour milk led to the preparation of baking powders. There are a great variety of them at present, but the underlying principle in all of them is the same. This is the formation of carbon dioxide from soda by the use of an acid salt or its equivalent. They all, therefore, contain sodium bicarbonate. In addition, one class, known as the *tartrate powders*, uses potassium acid tartrate, commercially called "cream of tartar." A second class, the *phosphate powders*, uses acid calcium phosphate; a third, usually called *alum powders*, uses aluminum sulphate. Besides these three classes there are many mixed powders, which usually contain mixtures of the second and third. In all cases starch or flour is added to the other ingredients to prevent chemical action taking place through exposure to the moisture of the air. The principle is the same as that employed in preventing common salt from becoming damp in wet weather.

3. **The Chemical Action.**—In the tartrate powders the reaction is shown by the equation,

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2.$$

It will be seen that the residue left in the baked product is potassium sodium tartrate, known as Rochelle salt. When phosphate powders are used the following reaction takes place,

$$4NaHCO_3 + CaH_4(PO_4)_2 \rightarrow CaNa_4(PO_4)_2 + 4H_2O + 4CO_2.$$

As will be seen, in this case a phosphate of sodium and calcium is left in the bread or cake, a compound not greatly different from the phosphate contained in the bones. With the alum powders the reaction is somewhat more complicated. Aluminum sulphate is not an acid salt and its action depends upon the complete hydrolysis of the aluminum carbonate and the instability of the carbonic acid formed. This will be made clearer by observing the equations below,

$$Al_2(SO_4)_3 + 6NaHCO_3 \rightarrow 3Na_2SO_4 + Al_2(CO_3)_3 + 3H_2O + 3CO_2.$$

This shows the results of the interaction of the two salts when brought together by the milk or water used in the dough. But it will be remembered that salts formed from weak acids with weak bases are completely hydrolyzed in water. Aluminum carbonate is such a compound. Hence, immediately a second reaction begins, thus,

$$Al_2(CO_3)_3 + 6HOH \rightarrow Al_2(HO)_6 + 3CO_2 + 3H_2O.$$

It will be seen from the equations that the carbon dioxide is evolved in two successive steps. In most of the alum powders, the soda is in such proportion as to furnish only about two-thirds as much available carbon dioxide as that given by the other powders; but to offset

this, the manufacturers claim that the evolution of the gas, in stages and not all at once, more than compensates for the smaller amount produced, in that the loss is much less in making up and handling the dough. It will be noticed that the two products which remain in the bread in this case are sodium sulphate and aluminum hydroxide. It must be remembered that baking powders are not used with sour milk, for the acid salt or the alum takes the place of the lactic acid and the different ingredients are so proportioned that at the close of the operation there shall be no excess of either. One or more well-known brands of baking powders incorporate with the other ingredients a small quantity of egg albumin. The claim of the manufacturers is that this increases the viscosity of the liquids used in making up the dough so that as a result the carbon dioxide will be retained the better. Carried out as an experiment in a test tube with water to bring about the reaction and no flour present, this is found to be true. But in the biscuit, itself, the claim is a very doubtful one. Suggestions have been made to use hydrochloric acid with soda as a leavening agent. Its reaction is

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

It shows that only common salt is left in the bread. The objection to this is that the hydrochloric acid is a liquid and therefore cannot be mixed with the soda beforehand. Each separate portion would have to be measured out at the time of using, so that the inconvenience might outweigh other considerations. The salt formed in a given quantity of bread is only about half what is ordinarily mixed with the flour; hence no objection could be offered in that respect. Scores of actual experiments with muffins, biscuits, every variety of cake and doughnuts, have been carried out by the author's

students using soda and hydrochloric acid, with uniformly successful results.

4. **Healthfulness of Baking Powders.**—Owing to the intense rivalry among the manufacturers themselves, the public has taken more or less interest in the comparative healthfulness of the various baking powders on the market. A general idea prevails that the tartrate powders are the most wholesome; this has come through unlimited advertising by the manufacturers of that class of powders. Food experts of the United States who have given special attention to the effects of adulterations and preservatives in foods unite in saying that *all* baking powders leave in the bread one or more substances classed as drugs, and since no efforts have ever been made to ascertain the effects in small quantities of these substances upon the human system, no one can say what the result is upon health. Inasmuch as the quantity consumed by any individual is not great, it is probable that the effects upon health are so small as to be negligible in the case of any of the powders. Moreover, other kinds of bread in which baking powders are not used seem to be gaining in use and popularity in America; hence, the discussion may well be left until it has been settled by actual experiment.

5. **Yeast Bread.**—A very considerable amount of the bread used at the present time, especially in cities, is what is commonly called "light bread" or that in which yeast is the leavening agent. Yeast is a microscopic plant which grows rapidly in a mixture of flour and water, if kept warm. As the growth proceeds, the sugar added and the starch which is changed into invert sugar as explained elsewhere, p. 220, are transformed into alcohol and carbon dioxide thus,

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

The equation showing the inversion of the starch is

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6.$$

When the dough has risen to a certain extent it is kneaded back; this breaks up the bubbles of gas into a very large number of small ones and gives a loaf of much more uniform texture. When heated in the oven the alcohol is expelled, since its boiling point is only 78°. The carbon dioxide is expanded so as to raise the dough and the yeast plants are killed. From the fact that large bakeries can control and maintain uniform conditions of temperature in their establishments, and more than this, can secure uniform quality of flour by blending if necessary, their product is fast supplanting that made in the home. It has been said before that it is the gluten that serves to hold the gas in the dough until the baking is completed. Naturally, therefore, a flour deficient in this respect will not rise well; one with too much will produce bread too light, with large pores. For this reason, up to within recent years, it was difficult for the housewife with different flours to make a uniformly satisfactory loaf, yet with no fault on her part. At present, all large flour mills have the wheat they intend buying tested as to percentage of gluten as well as in other respects. The flours they make are likewise tested. Thus with the composition known, a flour low in gluten may be mixed with one having a high percentage and both will be made right. At the present time, the output of flour is much more uniform than some years ago. This has resulted in large baking concerns themselves putting out a much more uniform product than was possible formerly. Since carbon dioxide in yeast bread is obtained through the decomposition of the starch, it will

be seen that there must be considerable loss in weight. In baking, including the water, which escapes, this is fully 15 or 20 per cent. It was estimated by Liebig, a German chemist, some years ago, that the alcohol produced in this way amounted in the German empire to twelve million gallons annually, and that the flour thus passing off into the air in gaseous form was sufficient for the bread required by an army of 30,000 men.

Formerly the housewife was dependent largely upon her own efforts for a continued supply of yeast. A piece of dough was saved each time and put away in a cool place until time for the next baking. Sometimes this was mixed with corn meal and dried, in which case it was good for several weeks or even longer. Later dry yeast was made an article of commerce and sold under the trade name of "Yeast Foam." At the present time "compressed yeast" which is a fresh and not a dried yeast has largely supplanted the dry form because of its very much more rapid growth when put into "sponge." Large bakeries use a yeast in a semi-liquid condition closely resembling thin batter.

6. **Salt Rising Bread.**—This special variety is made by mixing up a sponge of corn meal, and milk with some salt added, and allowing it to stand for some hours. Thereafter the procedure is not essentially different from that of ordinary bread. It is supposed that a special variety of yeast spore which grows rapidly in the corn meal mixture and which finds entrance from the air is the cause of the leavening and of the peculiar taste as well. Some few years ago this "wild yeast" was isolated by a graduate student at Kansas University, and salt rising bread may now be made with as much assurance of uniform results as with ordinary yeast.

7. **Aerated Bread.**—On account of the loss in weight in light bread as explained above, efforts have been made to force carbon dioxide into the dough mechanically, without the use of any yeast at all. This is done by putting the materials into large cylinders and pumping in carbon dioxide until a considerable pressure is reached. It is then kneaded mechanically by rotating the cylinders. After some time the dough is forced out, cut into suitable sizes and baked. The gas absorbed, having the pressure removed and the temperature greatly raised, expands in accordance with both Boyle's and Charles' laws and makes the product porous and light. The bread thus obtained is sweet and wholesome, but lacks the "yeasty" taste; it is more inclined to be dry than ordinary bread and has not been received well by the public.

8. **Beaten Biscuits.**—These were probably the original aerated bread. No leavening agent is used, but by continued kneading and "beating" more or less air is worked into the dough, which expands upon baking. Such biscuits are never as light as those made from soda or baking powder, but they retain all the relative, wholesome taste of the flour, with nothing objectionable or questionable added. The amount of time needed to make them is fast causing them to be an unknown article of food.

**Exercises for Review**

1. Explain the action of soda in making biscuits. Write the equation.

2. What prevents a gas escaping rapidly from dough? How may a sample be obtained for examination?

3. What difficulty is there in obtaining uniform results with soda?

4. Name the three classes of baking powders and give composition. What is the purpose of each ingredient in the baking powders?

5. What is left in the bread in the case of each baking powder?

6. Why can biscuit made from a baking powder never show an alkaline reaction?

7. Give advantages and disadvantages of using hydrochloric acid with soda as a leavening agent.

8. What may be said of the relative healthfulness of the various baking powders?

9. What is yeast? How does it leaven bread? Why were light breads in former years of such varying quality? Why more uniform now?

10. What can be said of the loss in making yeast bread?

11. What is aerated bread? How is the gas introduced into the dough? What advantages has it? Why has it not become popular?

12. How are beaten biscuits made? What disadvantage regarding them?

## CHAPTER XXVII

## THE CALCIUM FAMILY

**Outline—**

Members of the Group
Occurrence of Calcium
Properties of Calcium
Lime
  (*a*) Manufacture
  (*b*) Uses
Plaster of Paris
Cements
  (*a*) Natural and Portland
  (*b*) Concrete Work
Chalk
Calcium Chloride
Strontium and Barium

1. **Metals of the Group.**—The metals belonging to this group are calcium, strontium, barium and radium, ranging in atomic weights from 40 to 226. The first three react with cold water and form hydroxides, which are strongly alkaline although not very soluble. They are often called the *alkaline earth* metals.

2. **Occurrence of Calcium.**—Rocks containing calcium compounds are among the most abundant of the earth's crust. Limestone and the semicrystalline variety, marble, are both calcium carbonate as are also corals and shells. Limestone is produced by the cementing together of shells and similar material ground up by the action of the waves. Fossil remains of crinoid stems and brachiopods are commonly seen in ordinary limestone. The famous *coquina* rock, from which the old Spanish fort at St. Augustine in Florida was built, is made en-

tirely of coarse fragments of shells, firmly cemented together. Marble is usually more free from silica and other impurities than common limestone. It has been subjected to intense heat at some time in the earth's history such that it was softened and upon cooling became more or less crystalline in structure. Chalk beds are composed of the remains of the shells of microscopic animals, known as *globigerina.* In some parts of the ocean at the present time globigerina ooze is being deposited where chalk beds of a future day may be found. Calcium carbonate also occurs in crystals, often of considerable size, in the shape of flat rhombohedrons and sometimes in six-sided crystals, known as "dog-tooth spar." It is sometimes mistaken for quartz, but need not be, for its hardness is only three in the scale while that of quartz is seven. Gypsum, calcium sulphate, is also widely distributed. One very pure variety, known as *alabastine,* is often beautifully colored and is used for vases and similar wares. The native phosphate of calcium as well as feldspars containing calcium have been mentioned elsewhere.

3. **Description of Calcium.**—It has not been many years since calcium became an article of commerce, but it was first prepared more than a century ago by Sir Humphrey Davy, by methods similar to those he used for sodium and potassium. It is now made by electrolyzing melted calcium chloride, much as sodium is by the Castner process. It is a silvery white metal, resembling sodium, but much harder. It may be cut and worked much as lead may be. It reacts readily with water with the evolution of hydrogen; when heated it combines rapidly with chlorine, bromine and oxygen.

4. **Lime, CaO.**—This compound is made by calcining limestone in kilns. The native rock is heated strongly

with coke or wood for several days during which the carbon dioxide is expelled, thus,

$$CaCO_3 \rightarrow CaO + CO_2.$$

The better lime kilns are arranged so that the process is continuous. Limestone is fed in from above, while the finished product may be removed at the bottom. It is then shipped in barrels or loose to points where needed. Exposed to the air lime absorbs moisture and carbon dioxide and crumbles to a fine powder. Ultimately it becomes a carbonate again, so that the above reaction might be written

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

It reacts with water vigorously with the evolution of much heat. Use is made of this fact by balloonists as a means of securing heat at high altitudes without the use of fire. In case of considerable quantities of lime in contact with wood or other combustible material, the temperature reached, on the addition of water, is often sufficient to cause combustion. An illustration of this was seen at the time of the flood of the Kansas River at Kansas City in 1903, when many box cars loaded with lime were partially submerged in the freight yards. All of them took fire and burned to the surface of the water.

5. **Uses of Lime.**—One of the most important uses is for making mortar in building—foundations for houses, brick work, stone walls, and the like. For large buildings, cement is used because of its greater strength, but it will be seen later that cement contains a considerable percentage of lime. Mortar is made by mixing sand with slaked lime. When exposed to the air, as in the foundation of a building, chemical reaction with the carbon dioxide of the air takes place, the water is evap-

orated, and ultimately, if properly made, the mortar becomes a silicious limestone. Thus,

$$Ca(HO)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$

As the carbon dioxide in the air is limited in amount, the action is slow and probably continues for months or even longer. Moisture aids in the absorption. Slaked lime is often used to remove the hair from hides; boiled with sulphur it is used as a spray to prevent fungous destruction of peaches, plums, grapes and possibly other fruits. Molded into round sticks it is used in the calcium light, already mentioned on p. 68. It is also valuable as a whitewash for basements, board walls, trees and as a cheap disinfectant. Dilute solutions of the hydroxide are called lime water and are used in various ways in medicine. Milk of lime, which is water containing considerable calcium hydroxide in suspension is used with alum in settling the mud from river water for city supplies, also as a means of softening water, which will be explained later.

6. **Plaster of Paris.**—By calcining gypsum at such a temperature as to remove a portion of the water of combination, plaster of Paris is obtained. The reaction is

$$CaSO_4.2H_2O \rightarrow CaSO_4.H_2O + H_2O.$$

As put on the market it is a white powder. Its most remarkable property is that of being able to take up water and change back rapidly into the hydrated form again. This property is called "setting." If the quantity of water is not too great it takes place in a very short space of time. Examination with a magnifying glass shows the formation of a crystalline structure. In preparing plaster of Paris, if the calcining is continued sufficiently long to expel all the combined water, the product is called "burnt plaster" and has very little

value, for it takes up water again very slowly. Plaster of Paris is used in the finishing coat in plastering houses, for making plaster casts and statuary, in dental and other surgery, for interior raised decorations in large halls, panel work, as a filler for paper pulp, for school crayons, and in numerous other ways. When used in statuary, to prevent injury in washing, since calcium sulphate is somewhat soluble in water, the surface is usually treated with a solution of paraffin in naphtha or some similar volatile oil. Gypsum is often called "land plaster" and is frequently used as a corrective of alkalinity in soils.

7. **Cements.**—This class of complex substances may be divided into *natural* and *portland* cements. They all contain more or less lime, usually some magnesia, MgO, with silica, and aluminum oxide as the main ingredients. The first two of these are usually found together in what is called magnesium limestone; the others are obtained from shale, a hydrated aluminum silicate. When a quarry of rock contains all of these in such proportions as are more or less suited for the manufacture, the cement made therefrom is called a *natural* cement. However when the limestone is obtained from one quarry and the other rock from another, it is called a portland cement. This last name was given in England for the reason that when used the finished product resembled closely a special building stone known as Portland rock. Natural cements, as a rule, are comparatively high in the lime content. As this sets by the absorption of carbon dioxide from the air, such cements harden slowly. In preparing portland cement the separate portions are weighed in such amounts as have been found by experience to be best, are then calcined, mixed and ground to a fine powder. In the calcining two changes take place: the carbon

dioxide is expelled from the limestone and a part of the water from the hydrated shale. These steps, in a simple way, may be illustrated thus,

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2,$$
$$Al_4(SiO_4)_3nH_2O \rightarrow Al_4(SiO_4)_3mH_2O + xH_2O.$$

As plaster of Paris sets quickly through the hydration of the molecules, so any cement with the partially dehydrated silicate in excess will also. Since this is true of all portland cements, they harden rapidly even in the presence of much moisture and are for this reason often called *hydraulic cements.* For work in very cold weather cements with very high content of silicate are sometimes used; hence, they set before they have time to freeze. On the other hand, natural cements cannot be used under any such conditions or where much moisture will be present, as in piers for bridges, sewers, and similar places, for they set too slowly. Likewise, they cannot be used in large buildings, for the weight to which they are subjected before thoroughly hardened is sufficient to crush them.

Concrete is made by mixing cement, sand and crushed rock, often called "grits," in the proportion of 1, 3, and 5. Water is added and the whole rotated in a mechanical mixer till relatively homogeneous. This is then poured into position and allowed to harden. Thus are made roadways, sidewalks, foundations, bridge piers, and a vast number of other things. Much of the building in cities now is of *reenforced concrete.* This is made by putting iron rods into position and pouring the concrete mixture over and about them. For roadways, woven wire fencing is sometimes used. Floors of fireproof buildings and roofs, supported temporarily by false woodwork are thus made. The reenforcement enables the concrete to withstand any sudden shocks or great strain. The great

earthquake and fire resulting in San Francisco in the spring of 1906 gave great impetus to this method of building. It was found that the reenforced, fireproof construction was able to stand with relatively little damage even such terrible forces of destruction. During the last year of the Great War reenforced concrete was even used for a number of medium-sized ocean going vessels. Its uses are being extended more and more every year, since lumber is becoming more scarce. In 1915, government bulletins showed that there was an output in the United States of 90,000,000 barrels of cement, with great increases each year over the preceding. During the war this fell off some, because little building was done, but only temporarily.

8. **Prepared Chalk.**—Native chalk, it has been said, is formed from the minute shells of sea animals cemented together. It may be prepared artificially by treating a solution of some calcium compound with sodium carbonate in solution, thus,

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl.$$

The carbonate is a white precipitate; it is filtered out, washed, and molded into the desired shape or used as a powder. Properly made it is a perfectly smooth powder, entirely free from any gritty feeling. It is used in tooth powders and pastes, as well as in a variety of other ways in pharmacy.

9. **Calcium Chloride, $CaCl_2$.**—This compound is a white solid obtained as a by-product in the Solvay process of making sodium carbonate and in some other manufactures. For example,

$$2NH_4Cl + CaO \rightarrow 2NH_3 + H_2O + CaCl_2.$$

By evaporation of the solution thus obtained, the salt crystallizes out as a decahydrate, $CaCl_2 + 10H_2O$, which

is very soluble in water and hence very deliquescent. If heated strongly the hydrate loses all its water and becomes a dry, porous solid. It is this form which is most desirable for drying gases in the laboratory. A few cannot be dried this way, as they form molecular compounds resembling hydrates. For example, ammonia unites with the calcium chloride, eight molecules for one and forms a compound with the formula, $CaCl_2 + 8NH_3$. The crystalline variety is used in the brine tanks of many refrigerating plants instead of common salt. It is said to attack the metal pipes and boxes less than the sodium chloride does. Since a solution of calcium chloride may be made that will not freeze except at very low temperatures it has the advantage of being able to be transmitted considerable distances in refrigeration systems and still possess such a degree of cold as may be necessary. Since the supply of calcium chloride is greater than the demand, attempts have been made to find other uses for it. For preventing dust on roadways its use has been mentioned on p. 143. In many localities asphaltic petroleum is used. This prevents erosion by heavy rains, as well as by winds and heavy traffic. The calcium chloride cannot prevent damage by rains on account of its great solubility.

10. **Other Members of the Group.**—Strontium and barium occur in native compounds corresponding to those of calcium, the sulphate and carbonate. Barium sulphate, especially that made artificially, is used in many ways for adding weight. Paper pulp intended for cardboard and white paints often contain it as a filler, or adulterant.

The nitrates are both used in making fireworks and colored fires. *Fusees,* used upon railways to give warning of the nearness of another train, contain mixtures of strontium nitrate, shellac or sulphur and potassium chlo-

rate. The strontium compound gives the red color, the chlorate furnishes oxygen for rapid combustion, and the remaining portion is the fuel. Barium nitrate used in the same way gives a green fire. These were formerly used extensively for stage effects and still are where the electric spot light is not available. If to be burned indoors, shellac and not sulphur should be used on account of the fumes produced.

Strontium hydroxide, $Sr(HO)_2$, is used in the refining of cane sugar. It causes the separation of portions of sugar from the molasses after the main crystallization has taken place which would not otherwise be obtained. Barium forms both a monoxide, BaO, and a dioxide, $BaO_2$. The latter is of interest in that it may be used for the manufacture of hydrogen peroxide, thus.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2.$$

Barium hydroxide, $Ba(HO)_2$, is often used in the laboratory as a reagent instead of lime water.

### Exercises for Review

1. Name the metals of the calcium group. By what other name are they known?

2. Give some of the familiar natural compounds of calcium. What is coquina? Marble? Chalk? Alabastine?

3. How may calcite be distinguished from quartz when the crystals resemble?

4. How is calcium prepared? Describe the metal.

5. How is lime made? Equation?

6. Give the characteristics of lime.

7. Give important uses of lime. How does mortar harden? Show by an equation.

8. How is plaster of Paris made? What is its most remarkable property?

9. Give uses of plaster of Paris. What is land plaster?

10. Name the two classes of cements and state how each is obtained.

11. What advantage has portland over the other? Can you think of any reason why the natural might be preferred?

12. What is concrete? How does it harden? What is reenforced concrete?

13. How is prepared chalk made? Give uses.

14. What is the source of the calcium chloride of commerce? What two varieties? Explain the difference between them.

15. Give some valuable uses for calcium chloride.

16. Give some uses for the nitrates of strontium and barium. Why are they so used?

17. Name some other compounds of barium and strontium that are of some use.

18. Complete these equations, using amounts needed,

$$Ca(NO_3)_2 + Na_2CO_3 \longrightarrow ,$$
$$Ba(HO)_2 + HCl \longrightarrow ,$$
$$SrCO_3 + HNO_3 \longrightarrow ,$$
$$Sr(NO_3)_2 + NH_4HO \longrightarrow .$$

## CHAPTER XXVIII

## HARD WATERS—METHODS OF SOFTENING

**Outline—**

Kinds of Hard Waters
Effects of Hard Waters
Treatment for Hardness
(*a*) In the Home
(*b*) For Commercial Enterprises
Effects of Coagulants upon City Supplies
Hardness as Related to Soap
Method of Estimating Hardness

1. **Kinds of Hardness.**—Any water containing mineral matter in solution which will cause a precipitate with a soap solution is said to be *hard.* The soap solution must be perfectly clear: when added, the formation even of a slight cloudy appearance shows that the water is distinctly hard. More often hardness is caused by the presence of calcium or magnesium salts, but occasionally by iron. When the hardness is such that boiling will remove it, it is said to be *temporary;* otherwise it is *permanent* hardness. This does not mean, however, that there is no possible way of removing it. Both kinds of hardness may be present and often are. Temporary hardness is caused by the presence in the water of the acid carbonate of calcium or magnesium, often called the bicarbonate, $CaH_2(CO_3)_2$. When boiled, decomposition takes place, with the formation of the normal carbonate. This being insoluble in water precipitates out, thus,

$$CaCO_3.H_2CO_3 \rightarrow CaCO_3 + CO_2 + H_2O.$$

It is the compound, $CaCO_3$, which collects upon the inside of teakettles as a rough deposit, also in the hot water coils

in furnaces and water heaters, and in all steam boilers which use hard water. It is one of the greatest annoyances with which the engineer has to deal as well as one of great expense. All sorts of "water softeners" have been put upon the market under various names, many of them worthless. Fig. 62 shows two actual cases of sections of pipe taken from two manufacturing plants, which show that the "boiler scale" as it is called had nearly closed the pipes. It is said that a layer ¼ inch in thickness lessens the heating effect by half, or in other

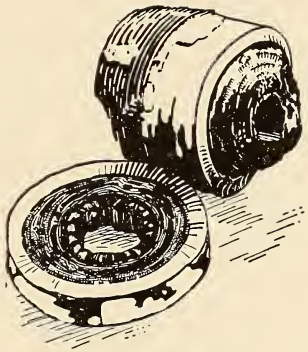


Fig. 62.—Scale in iron pipes, from an actual case.

words it is the equivalent of an iron pipe 5 inches in thickness. In the cases shown in Fig. 62 the scale was about ¾ inch thick. Under such conditions, in gas heaters or furnace coils, in the home, the water in the tank is warmed very slowly, while the iron of the pipe is being rather rapidly burned away. Finally, it becomes so thin that under the water pressure it bursts, and must be renewed.

Permanent hardness is caused usually by the presence of sulphates of calcium or magnesium, although the chloride, especially of magnesium, may be the cause. As these

compounds are not decomposed at the temperature of boiling water, they remain in solution.

2. **Removal of Temporary Hardness.**—Since temporary hardness is caused by the presence of an acid salt, it would seem that naturally an alkali would remove it. For laundry and bath purposes at home, dilute ammonia water is thus often employed. The reaction is shown by the equation,

$$CaCO_3.H_2CO_3 + 2NH_4HO \rightarrow CaCO_3 + (NH_4)_2CO_3.$$

As the calcium carbonate is not soluble in water it settles to the bottom and leaves the water soft. The ammonium carbonate, unless present in large quantities has little effect upon the soap, hence is not objectionable. If much water is to be treated, this method is too expensive. Therefore, steam laundries, many of which use from 50,000 to 100,000 gallons of water per day, and other similar establishments, must employ a cheaper alkali. The cheapest known is lime water, and this is used. Daily analysis of the water is made so as to know exactly the amount of hardness present. This being known, into large settling tanks, holding sufficient for a day's run, milk of lime is added sufficient to combine with the acid carbonate and convert it into the normal salt. This reaction takes place,

$$CaCO_3.H_2CO_3 + Ca(HO)_2 \rightarrow 2CaCO_3 + 2H_2O.$$

The precipitated carbonate settles to the bottom and is then drawn off to the sewers. Lime water cannot be employed in the home because the quantity of water used is relatively small and any excess of the reagent would leave the water as bad or worse than before. Many cities, with river water more or less muddy, use milk of lime as already mentioned on p. 45 in removing the turbidity. Not only does it accomplish this, but to

prevent any excess, even minute, of the alum or whatever is employed as a coagulant, a very slight excess of lime is used. This reacts, as shown above, with the precipitation at least of a portion of the temporary hardness. In such treatment of water, however, for turbidity, the permanent hardness is always increased as the equation will show,

$$Al_2(SO_4)_3 + 3Ca(HO)_2 \rightarrow 3CaSO_4 + Al_2(HO)_6.$$

The aluminum hydroxide is the gelatinous coagulum which drags down the mud, but the calcium sulphate is soluble to a degree and in this way adds to the permanent hardness as stated.

3. **Removal of Permanent Hardness.**—For removal of this in large plants the water is treated with the requisite amount of sodium carbonate in solution. This reaction then takes place,

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4.$$

The sodium carbonate is added at the same time as the milk of lime previously mentioned. The precipitate, it will be noticed, is the same as in the other case; both will settle together and be removed at the same time. Sodium sulphate in this case remains in the water, but in small quantities causes no appreciably bad results. In large amounts *any* sodium salt would cause the precipitation of the soap when added, from ionic reasons. This was found true when hydrogen chloride was passed into a solution of common salt to produce pure sodium chloride. (See p. 309.)

**The Permutit System.**—This is sometimes called the zeolite process, and is protected by rigid patents. The water containing the calcium or magnesium compounds is made to flow through cylinders containing an artificial sodium compound known as *zeolite*. In the process the

magnesium and calcium in the hard water are removed by interchange with the sodium in the zeolite. It is said the water is rendered perfectly soft. In the case of very hard waters, however, considerable amounts of sodium salts are introduced into the softened water. As this is objectionable, the water must be further treated with lime as described already.

4. **Effects of Hardness upon Soap.**—Without the softening of the water used in large plants, the cost of the soap item would be enormous. No work can be done by soap as long as the water is hard, for it reacts with the compounds of calcium present thus,

$$CaSO_4 + 2NaC_{17}H_{35}COO \rightarrow Na_2SO_4 + Ca(C_{17}H_{35}COO)_2.$$

The equation shows by the interaction that a calcium stearate is formed, a species of soap, which is insoluble in water, and *floats*. It forms the disagreeable, greasy-feeling scum upon such waters and adhering to the sides of the bath tub. In laundry work it sticks to the clothing and under the hot iron it melts like wax and is thus spread out upon the garment as a dark gray or dirty looking spot. So with hard water, aside from the expense, high quality work in a laundry is impossible. When the soap has combined with all the calcium salts present in the water then it can begin to form emulsions for the removal of the foreign matter from the clothing, but not before. In all cities using hard water the soap bill is a constant tax upon the people. In Glasgow, Scotland, a few years ago, a change was made from the hard water supply which had been used for years to one much softer. In the first year the saving in soap bills was estimated at $200,000. In the home, therefore, if the water is appreciably hard, small quantities of sal soda with very little ammonia water should be used both as a means of economy and for better results. Borax, as a water softener, when delicate

garments are to be laundered or for washing the hair, is regarded as preferable to sal soda. Its reaction upon the hard water is not essentially different from that of the soda, except that the calcium is changed into a borate instead of a carbonate, thus,

$$Na_2B_4O_7 + CaSO_4 \rightarrow CaB_4O_7 + Na_2SO_4.$$

5. **Degree of Hardness.**—Hardness in water is estimated in *degrees.* Thus, water which contains 1 grain, or about $\frac{1}{15}$ of a gram, in a gallon, of calcium carbonate or its equivalent of any other calcium salt is said to have one degree of hardness. This is about the equivalent of one part of calcium carbonate in 50,000 or 60,000 of water. For every hundred gallons of water with one degree of hardness, between 2 and $2\frac{1}{2}$ ounces of soap must be used simply to remove the hardness before doing any cleansing. Not only is this much soap wasted, but the greasy precipitate gathers upon the clothing as mentioned. For a family of four it is estimated that about 16 pounds of soap would be required in a year to soften the water alone. Hardness sometimes reaches as high as ten or even twenty degrees in which case the soap used is no small item, when the laundry work is done at home. If treated with sodium carbonate, a little over $\frac{1}{2}$ ounce is sufficient to remove one degree of hardness from 100 gallons of water; 5 or 6 pounds would be sufficient for laundry and bath purposes for a whole year. With ten degrees of hardness 50 to 60 pounds would be needed. Since a pound of sal soda is very cheap it becomes a matter of great economy to soften the water thus before adding the soap.

### Exercises for Review

1. What is meant by hard water? What two kinds are there? Explain the difference?

2. Can water be both temporarily and permanently hard? Explain.

3. What produces temporary hardness? Permanent?

4. What is boiler scale? Show by an equation how it forms.

5. How may temporary hardness be removed at home? On a large scale how is it done?

6. What is the effect upon city waters of removing the mud by a coagulant?

7. How do laundries soften the water for their work? Show by equations how they remove both kinds of hardness.

8. What is meant by one degree of hardness? How high may water run?

9. State effect of great hardness upon cost of living.

10. What is the effect of hardness upon soap? What unpleasant results follow the use of soap in hard water?

11. Complete these equations:

$$CaH_2(CO_3)_2 + \text{soap} \longrightarrow ,$$
$$CaSO_4 \text{ (heated)} \longrightarrow ,$$
$$CaSO_4 + NH_4HO \longrightarrow ,$$
$$CaSO_4 + Ca(HO)_2 \longrightarrow ,$$
$$CaH_2(CO_3)_2 + NH_4HO \longrightarrow ,$$

In which of these five equations is the water softened and in which not?

# CHAPTER XXIX

## CLEANING AND POLISHING

**Outline—**

Necessity for Cleanliness
Solutions and Emulsions
Cleansing by Soap
    Chemistry of
Dry Cleaning
Sinks and Waste Pipes
Cleaning Metal Wares
    (*a*) Silverware
    (*b*) Copper and Brass
    (*c*) Aluminum Vessels
    (*d*) Nickel

1. **Importance of Cleanliness.**—The great problem of modern civilized life is that of cleanliness. It is the one great contributing factor of health. Formerly soap was used largely as a medicinal preparation and not as a detergent. Real cleanliness was almost unknown and impossible: epidemics swept unchecked through communities. Perfumes were adopted as disguise for lack of cleanliness.

2. **Emulsions and Solutions.**—If a little oil be shaken in a test tube with some ether, the oil disappears and we have a homogeneous mixture which is called a solution. If the experiment be repeated with oil and water, the two may be mixed by vigorous shaking, but the oil soon separates out and rises to the top. Again, if some soap be added to the oil and water in the tube and shaken for some time, the oil disappears and only separates out again very slowly. Moreover, the resulting mixture has become cloudy or even milky in appearance.

It is called an *emulsion*. Milk is probably the most familiar example of emulsions and the oil in the form of cream only slowly rises to the top.

3. **Cleansing Action of Soap.**—Just what is the action of soap in cleansing by means of it is somewhat a matter of question. As a rule "dirt" or foreign matter adheres to clothing or to the body because of oily matter present. "Clean" mud when dry may be easily brushed off, but mixed with grease it cannot. If in some way the oil or grease may be removed, then the dirt is carried away mechanically by the water. But oils are not soluble in water, hence cannot be removed thus. Hot water may melt the grease and cause more or less of it to float away, but even this is imperfect. The use of soap is the most common method. It has been seen that in water soap is hydrolyzed with the formation of some sodium hydroxide. It is believed by some that this free alkali, especially if the water be warm, saponifies the oil upon the garment or body, and that the water then dissolves and carries it away together with the dirt. This may occur to some extent, but the process of saponification is too slow, apparently, to account for all that happens. What seems more probable is, that the soap forms an emulsion with the oil and that it is thus removed together with the associated foreign matter. This process is fairly rapid. In accordance with this idea and to aid in the emulsifying of a solid fat there are soaps on the market which contain a considerable percentage of naphtha or some other oil. In laundry work the naphtha is believed to dissolve the grease on the garment and then the liquid emulsifies more easily with the soap. Very hot water is not desirable in the use of such soaps as they tend to evaporate the naphtha before it has dissolved the grease. Upon cotton goods soaps with not

over 1 per cent of free alkali may be used without serious results; for woolens and for toilet purposes there should be none present. For rough cleaning, as of floors, unfinished, free alkali in soap is not objectionable, but upon painted or varnished surfaces it is injurious.

4. **Dry Methods of Cleaning.**—Sometimes the nature of the fabric does not admit of the use of soap and water. In such cases, sometimes, it is possible to remove the grease by heat and an absorbent. Below the spot is placed a sheet of blotting paper or Fuller's earth, or French chalk, or some similar porous agent. A hot iron applied above will melt the grease and tend to expel it. Then it will be largely taken up by the absorbing agent. In ordinary *dry cleaning* a volatile solvent is used. The oil is dissolved out of the garment and the foreign matter washed away mechanically. Ether is one of the most excellent solvents known for oils and fats, but it is too expensive for ordinary use; moreover, it is very inflammable. Carbon tetrachloride is also an excellent solvent for oils, and is not inflammable, hence perfectly safe. It is more expensive, however, than some other agents. Benzine and gasoline are both good solvents for oils and are the most commonly used on account of their cheapness. However, they are very inflammable, and carelessly handled are the cause of many explosions and fires.

Painters and workmen about oily machinery ordinarily remove the dirt from their hands, first by some solvent. Kerosene or gasoline upon "waste" will dissolve the linseed oil in the paint or the grease as the case may be, and soap will finish the process.

5. **Ink and Other Stains.**—Ordinary black ink since it is made from green vitriol and nutgalls may be removed by applying a solution of oxalic acid in water. Usually a few minutes is sufficient. The spot should

be washed with water afterward. Other black inks may generally be removed from clothing by moistening the spot with a solution of bleaching powder in water. After allowing to stand a few minutes, add vinegar and wash with water. Violet and other anilin inks may usually be removed with bleaching powder solution without great difficulty. But it must be remembered that this method cannot be used upon a colored article, as it will be bleached.

From the common use of red ink in bookkeeping accidents sometimes occur. For the removal of such stains a mixture of about twenty parts of denatured alcohol with one of nitric acid is recommended.

Iron rust may generally be removed by moistening with citric acid or lemon juice and exposing to bright sunlight. Usually one treatment is sufficient. Indelible inks, which usually or often contain silver nitrate, may be removed by a solution of ammonium chloride and corrosive sublimate—10 grams of each in 80 c.c. of water. This should be rubbed on with a soft cloth. Lunar caustic stains upon the hands may thus be removed.

Fresh paint upon clothing may be removed by applying turpentine or benzine, better with a cloth or blotter beneath to absorb the oil. Old or dried paint on woodwork may be removed by applying a mixture of aqua ammonia and a 25 per cent solution of sodium hydroxide, one part each, with five parts of water glass. Allow it to remain on the wood till the paint has softened, then wipe off.

Pencil marks and soiled spots upon tracing cloth may be wiped off with benzine upon a soft cloth, without affecting the ink drawing at all. Oily stains upon wall paper may often be removed by applying a paste of kaolin and water or magnesia in benzine and allowing

to remain about twelve hours. Then rub off gently with a soft cloth. Sometimes a second application is necessary.

Nitric acid stains upon the hands are very difficult of removal. One of the best plans is to apply a strong solution of potassium permanganate and after a few minutes wash off with hydrochloric acid, about 5 per cent in strength.

6. **Cleaning Waste Pipes.**—It often happens that waste pipes from kitchen sinks becomes more or less clogged so that water is only carried away slowly, if at all. This is usually largely the result of carelessness. The grease removed from the dishes by hot water and soap becomes solid again when the water is cooled in the trap, and adheres to the waste pipe. If coffee grounds or other similar solids are poured into the sink they are caught by the grease and in course of time fill the trap and waste pipes. If care is taken never to put any such solid material into the sink there will seldom be any trouble. The grease may solidify upon the pipe but the alkali formed by the hydrolysis of the soap and from the washing powders will gradually saponify it and remove it. Especially will this be true if occasionally a spoonful or two of some washing powder be dropped into the strainer of the sink and allowed to stand in the trap over night. In very bad cases some caustic soda or lye dropped upon the strainer and left over night will generally open up the pipe so that warm water will clean it out, without the aid of the plumber.

7. **Cleaning Metal Surfaces.**—Most metals exposed to the air if moisture be present become tarnished either through the action of the oxygen or because of some other gas present in the atmosphere. Upon articles commonly used in the home this action is relatively slow

as a rule, so that only in the course of weeks does it become appreciable. In the case of silverware, the coating is a sulphide; usually with other metals it is some form of oxide. Obviously, anything which would dissolve the oxide, or sulphide, would remove it and leave the surface as bright as before. Frequently, however, a reagent that will dissolve the film will also react with the metal itself. Hence, great care must be exercised in the use of such cleaning agents. In the case of silverware, the sulphide coating is readily soluble in a solution of potassium cyanide and may be quickly removed in that way. But since potassium cyanide is a most violent poison, its sale is restricted and this method is not suited to the home. All small silver articles, such as knives, forks and spoons, may be readily cleaned by putting them into some aluminum vessel, covering with water and warming for a few minutes. Some think the addition of a little salt is helpful. As aluminum is much more electropositive than the silver, the sulphur is thus removed from the less positive metal and it is left clean and bright. There are many silver polishes to be had on the market, but they require more work and time and are more harmful to the silverware. A home-made powder, which is good and harmless, may be made of the following common substances,

Prepared chalk, 3 parts,
Tartaric acid, 3 parts,
Powdered alum, 1 part.

Oxalic or citric acid may be substituted for the tartaric. The oxalic is usually the cheapest. Lemons contain citric acid. All must be finely powdered and well mixed together. The mixture is to be applied with a soft, damp cloth.

8. **Copper and Brass.**—The film of oxide upon copper and brass articles is soluble in ammonium hydroxide. Usually, therefore, polishes made for such surfaces contain some ammonia. Venetian red, rouge, whiting, or any similar powder, mixed with water and a little ammonia work well upon these metals. It is necessary in using such a polish, to wipe the surface perfectly dry and clean at the close, for the alkali also attacks the metal and if left would cause it to tarnish again and quickly. Polished brass articles are usually protected by a thin coat of lacquer. This is made by dissolving shellac in alcohol. It is applied by means of a soft brush.

9. **Aluminum Ware.**—Kitchen ware made of aluminum does not tarnish readily, and usually nothing more than ordinary cleanliness is needed to keep it in good shape. Putty powder, whiting or rouge mixed with a little oil are good for polishing if needed. The addition of some organic acid like the juice of lemon or oxalic may be helpful. Strong alkalies attack aluminum readily; hence, washing powders that contain free sodium hydroxide, as many of them do, should be used only sparingly and not left to stand in the vessel.

10. **Nickel and Other Metals.**—Nickel plated surfaces may be cleaned by polishing with whiting or rouge, mixed with some organic acid. Vinegar or oxalic are good. Iron vessels are so readily attacked by oxygen in moist air that they are not used unprotected. The various methods for preserving such surfaces are mentioned elsewhere. For tin cans, tin plate is used, for which, see page 403. For larger articles, steel plate is galvanized, mentioned on p. 384. For cooking vessels much "granite ware" is still used. Kitchen stoves are protected often by enamels, baked on at intense heat.

These may gradually wear off, when they should be replaced by a prepared article to be had at hardware and automobile supply houses. Heating stoves are usually protected by a thin film of magnetic oxide of iron, put on by treating the metal with superheated steam. This gives the surface a bluish color. It is sometimes spoken of, in the case of stove-pipe especially, as "Russia iron." This film adheres firmly and is fairly durable. Such surfaces do eventually rust, however. Prepared polishes usually containing graphite, are applied and polished by rubbing briskly with a stiff brush. Liquid polishes are to be had which dry with a gloss and need no rubbing, but often they burn off at the first heating and are of little value.

### Exercises for Review

1. What is an emulsion? How is it different from a solution? Illustrate.

2. Name some very common emulsion. How may an emulsion of soap and kerosene be made?

3. Give the cause for dirt adhering to clothing. What is the theory underlying the cleaning of clothing?

4. Give two theories regarding the cleansing action of soap.

5. Which is the more plausible of these theories? Wherein lies the value of a soap containing naphtha?

6. Why are soaps with free alkali objectionable with woolens? Why do they make the hands chap?

7. Describe one method of removing a grease spot from a garment by heat.

8. Give the usual method of dry cleaning. What is the principle involved?

9. Name the solvents that might be used in dry cleaning. What advantage has each? Why is benzine commonly used?

10. What is the best means of cleaning the hands when badly soiled by working about machinery?

11. What kinds of soaps should be used upon finished woodwork, if any? Why do you say so?

12. What is usually the cause of stoppage in wastepipes in kitchen sinks? How may they be kept clean?

13. If already stopped, how may a waste pipe as a rule be opened?

14. What is the cause usually of metals tarnishing? What in the case of silverware?

15. Give some easy way of cleaning small articles of silver. Explain the chemical action.

16. How is brass usually protected against tarnish? What do most copper and brass polishes contain? Why?

17. Why do tomatoes, rhubarb, and similar articles of food tend to keep aluminum cooking vessels bright? Why should strongly alkaline washing powders not be used much upon aluminum ware?

18. How may one know by the feeling in water whether a washing powder contains much free caustic soda?

19. Name some ways of protecting the iron used in the home. What is Russia iron? How are stoves usually polished? Why is this substance commonly used?

# CHAPTER XXX

## THE COPPER GROUP

**Outline—**

Members of the Group
Copper
(*a*) Occurrence
(*b*) Characteristics
(*c*) Uses
(*d*) Alloys
Compounds
(*a*) Blue Vitriol
(*b*) Other Compounds
Silver
(*a*) Occurrence
(*b*) Characteristics
(*c*) Uses
(*d*) Compounds
(*a*) Silver Nitrate
(*b*) Silver Chloride
(*c*) Silver Bromide
Photography
(*a*) Principles Involved
(*b*) Developing
(*c*) Printing
(*d*) Kinds of Papers
(*e*) Blue Prints
Gold
(*a*) Occurrence
(*b*) Methods of Mining
(*c*) Characteristics
(*d*) Uses

1. **Members of the Group.**—To this group belong three metals all of which are found free in nature. For this reason they have been known from most remote times. Moreover, all are soft metals, hence easily worked even

without any great advancement in scientific processes. They are often spoken of as the "noble metals," a term applied to all which may be separated from their ores by heat alone. In the periodic table they are found at the left hand in the same division as sodium and potassium. It will be noticed, however, that they are placed on the right side of this column and not under the alkali metals. In the study of the table it was said that the metals seemed to arrange themselves in octaves and that those with the same properties occur at intervals of eight. It should be added here that after we pass potassium, these periods become *double* octaves; that is, leaving potassium, a single octave brings us to copper which is so different from the alkali metals that it was placed at the right of the space as a member of another family; again proceeding, another octave brings us to an alkali metal which is placed under sodium. In this way, copper, silver and gold are at the center, as it were, of three *long periods* or *double octaves,* and are classed together. In many ways they are alike; in other respects, they are dissimilar; but in nearly all their properties they are utterly unlike the alkali metals. Silver has a valence of one; copper is usually regarded as bivalent, although it forms unsaturated compounds where it appears as if univalent. Gold is trivalent, but forms one or more compounds in which it appears as if univalent. They are all malleable, ductile, and good conductors of electricity.

2. **Occurrence of Copper.**—By the Greeks and ancient Phoenicians copper was obtained from the mines upon the island of Cyprus. This gave the metal its name, *cuprum,* from which it derived the symbol. In America the longest known deposits are those of the Lake Superior and Michigan regions. From copper vessels found in the mounds of prehistoric tribes it is known that they were

familiar with these deposits. The outcropping metal was in thin sheets between layers of rock. By cracking this off, sometimes by heavy stones, sometimes apparently by fire, the thin sheets were obtained and beaten into rude vessels. These deposits are still valuable and some of the mines as the Calumet and Hecla, though at a depth of a mile or more, are still heavy producers. The copper in this region is mostly pure and is separated from the rock mechanically.

*Western Deposits.*—In several of the western states, especially Montana, Colorado, Arizona and New Mexico, copper occurs mostly in the form of compounds of great variety. Many of them are sulphides having different content of sulphur, and known under a variety of names. Such are bornite, copper glance, peacock ore, and calchopyrite. Two basic carbonates, called *azurite,* deep blue in color, and *malachite,* a deep green, are known.

3. **Characteristics of Copper.**—Copper is a red metal with a specific gravity of about 11, and melts at a temperature of about 1,090° C. It tarnishes somewhat in damp air, but since the film of oxide adheres firmly to the metal the oxidation is merely superficial. In the presence of much moisture carbon dioxide is also taken up from the air forming a greenish compound of basic copper carbonate. It is a very tenacious metal, malleable and ductile. Wires may be made of a diameter but little greater than 1/1000 of an inch of which a length measuring a half mile would only weigh about 5 grams. It does not decompose either sulphuric or hydrochloric acids in the cold, for the reason that it is well down the electromotive series of metals as shown on p. 65. It does decompose nitric acid rapidly, because of its ready union with oxygen. It is an excellent conductor both of heat and electricity.

4. **Uses of Copper.**—Copper has many and varied uses. Because of the fact that it tarnishes only on the surface it is valuable for cornice work, roofing and guttering and is frequently so used. For the same reason it is often used as a covering for hulls of vessels. Its great conductivity for electricity together with its tenacity gives it use for wiring houses for electric lighting, for telephone circuits and a great variety of other electrical uses. Being an excellent conductor of heat renders it valuable for stills and boilers, and for cooking vessels. It is almost universally used in candy factories, for the reason that the syrup scorches much less readily in a copper vessel than in most others. This is because the heat is distributed quickly and evenly over the surface, while in an iron vessel, or one of porcelain ware, the bottom is very much hotter than the sides. In large establishments where great quantities of food must be prepared as in asylums and penitentiaries, or in restaurants like the railway eating houses where the service must be very rapid, copper vessels are used almost exclusively. Such vessels would probably find use also in the home were it not for the fact that, while such strong acids as sulphuric and hydrochloric are not decomposed by copper, it does react with many fruit acids, such as those found in tomatoes, apples and the like. Since the compounds resulting are poisonous, it is not desirable. In large establishments, such of the vessels as are used with acid foods are "tinned" on the inside. As this wears off it has to be replaced. In the form of alloys, copper is used in large quantities. Gold and silver coins are 10 per cent copper; brass contains zinc and copper, a common variety having 65 per cent of the former to 35 of the latter. Bronze consists of copper and tin; German silver of copper zinc and nickel.

5. **Blue Vitriol.**—This compound of copper, often called *blue stone,* is mainly a by-product of the large gold and silver refineries. Small portions of copper in the form of a sulphide occur mixed with the other metals; in a specially constructed furnace to which air is admitted the copper sulphide is oxidized to copper sulphate. This is treated with water and dissolved out, is filtered and evaporated to the point of crystallization. Formerly, a very considerable portion of that used in the United States was made in the Argentine smelter at Kansas City, with a monthly output of 1,800 tons. After the consolidation of the various refining companies, this work was transferred to the plants at Omaha and Denver. Blue vitriol crystallizes with five molecules of water. Exposed to the air it gradually loses this, becomes white and crumbles to a powder. By adding water the color is restored, and upon crystallizing the pentahydrate is again obtained. Its solution gives an acid reaction with litmus owing to hydrolysis. (See p. 313.) Like other salts of copper it is very poisonous.

6. **Electrotyping.**—Blue vitriol is used extensively in making electrotypes for printing books and magazines. The type is set up, proof read and locked in a frame or "form" the size of the page to be printed. An impression of this is taken in a sheet of prepared wax and this is covered with finely powdered graphite to make it a conductor of electricity. This is then suspended at the cathode in a solution of blue vitriol. A sheet of copper forms the anode (Fig. 63). When the battery is connected, copper is slowly deposited upon the graphite covered face of the wax. When the deposit has attained the thickness of a good visiting card, the sheet is removed from the solution, washed thoroughly and dried. Molten type metal is then poured upon the back of the

copper. This melts off the wax and gives a copper plate the exact duplicate of the lead type used to make the imprint upon the wax. All books are printed from such *electrotypes;* likewise, "patent" advertisements which are run in the large dailies of all the cities, and wherever a very large number of copies is desired. Lead type is so brittle that it will permit of only a relatively limited number of impressions with perfect results. By a similar method is made pure *electrolytic* copper for which in limited amounts there are many demands. To obtain this the impure copper is suspended from the

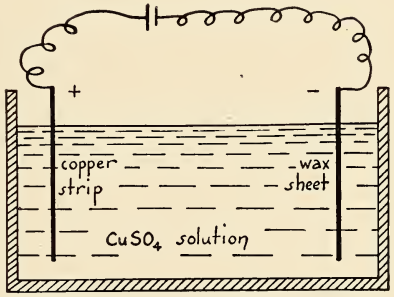



Fig. 63.—Making an electrotype.

anode and a very thin sheet of pure copper at the cathode. As the copper ions from the blue vitriol solution deposit upon the thin sheet at the cathode, the sulphate ions dissolve the impure copper bar at the anode and thus keep the vitriol solution concentrated. Thus, gradually, all the copper at the anode may be transferred to the cathode where it is deposited pure electrolytic copper, while the impurities remain in solution or precipitate out. Blue vitriol has also found wide use in "crow-foot" and other similar wet batteries for telegraphic work; its use in preventing the growth of algæ in water reservoirs has been

mentioned. It is also used extensively for making bordeaux mixture for spraying trees.

7. **Some Other Compounds.**—Copper forms many other salts; for example, cupric chloride, $CuCl_2.2H_2O$ of a beautiful turquoise blue color; cupric nitrate, $Cu(NO_3)_2.6H_2O$, dark blue in color, and very deliquescent; copper acetate, $Cu(C_2H_3O_2)_2H_2O$, green in color. It also forms cuprous salts, such as cuprous chloride, $Cu_2Cl_2$, white in color, and very unstable. In the presence of air and moisture this rapidly takes up oxygen and forms a basic cupric chloride. There are two oxides, cupric and cuprous, with the formulas, CuO and $Cu_2O$. The former is black and the latter red in color.

8. **Occurrence of Silver.**—Silver is often found free, sometimes in nuggets of considerable size. Most copper ores contain more or less silver, but the greater part of our supply is obtained from the lead smelters in the treatment of argentiferous lead ores.

9. **Characteristics of Silver.**—Silver is one of the whitest of the metals and the best in conductivity. It has a melting point of about 960° C., a little more than 100 below that of copper. It does not oxidize in the air at any temperature, but readily reacts with hydrogen sulphide. As this frequently occurs in the air from the combustion of coal or coal gas, or from the decomposition of various proteins containing sulphur, silverware commonly becomes tarnished. While silver will not *combine* with oxygen even at high temperatures, above its melting point, it will *absorb* more than twenty times its own volume of oxygen from the air. When solidification takes place this occluded oxygen is given off again rapidly, causing the silver surface to "spit" and become rough. It is even more ductile than copper, such that wires a mile and a quarter in length will weigh only about

1 gram. Silver is not attacked by alkalies or by hydrochloric acid or cold sulphuric. Nitric acid is readily decomposed and also boiling-hot, concentrated sulphuric.

10. **Uses of Silver.**—Everyone is familiar with the uses of silver. Thermos bottles and Dewar bulbs, mentioned elsewhere, and the better class of mirrors are silvered by the reaction of a reducing agent with a silver salt. Formaldehyde or Rochelle salt in the presence of an alkali is often used for this purpose. The process may be easily illustrated. If a few cubic centimeters of a solution of silver nitrate be put into a test tube and ammonium hydroxide added drop by drop until the brown precipitate which forms at first is just dissolved, upon adding a little tartaric acid and warming, the tube on the inside is beautifully silvered. Our silver coins are 90 per cent silver. "Sterling" silver does not mean, as many suppose, pure silver, but of the same degree of fineness as English coins, which are 925 parts of silver to 75 of copper. Most of the silverware in common use is merely some harder metal or alloy plated with silver. The process is the same as that described for copper plating. A sheet of silver is suspended at the anode and the article to be plated at the cathode. A solution of potassium silver cyanide takes the place of the copper sulphate. In the case of silver, the nitrate, the most common silver salt, does not give a deposit that adheres well.

11. **Silver Nitrate, $AgNO_3$.**—This compound may be prepared by dissolving silver in nitric acid. Nitric oxide and water are the two other products formed, as is usually the case when a metal decomposes nitric acid. This is seen in the equation,

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

Silver nitrate crystallizes in thin, flat plates, rhombic in

shape, colorless and transparent. Commercially, it is sold for medical purposes in small round sticks under the name "lunar caustic." These usually contain a small percentage of silver chloride. It has caustic properties and is used for this reason in cauterizing wounds, such as dog bites, and others presumably infected. In solution it is sometimes used for sore throat and otherwise as an antiseptic. Exposed to light, especially in contact with organic matter, it turns dark. On this account it is a constituent of many indelible inks used in laundry marking; also of most hair dyes, and as the source of the silver compounds used in photography.

12. **Silver Chloride, AgCl.**—If a solution of common salt be added to one of silver nitrate, silver chloride is produced, thus,

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3.$$

It is a curdy white precipitate, especially if shaken vigorously; it rapidly turns dark when exposed to sunlight. It is very soluble in ammonium hydroxide, forming a complex silver salt resembling the hydrates. Thus,

$$AgCl + 2NH_4HO \rightarrow AgCl.2NH_3 + 2H_2O.$$

Silver chloride is used extensively in preparing one class of photographic papers which will be studied later.

13. **Silver Bromide, AgBr.**—This compound is made by adding to a solution of silver nitrate one of potassium or ammonium bromide, thus,

$$AgNO_3 + NH_4Br \rightarrow AgBr + NH_4NO_3.$$

It is a very pale-yellow precipitate, much less soluble in ammonium hydroxide than is the chloride. It is much more sensitive to light. For this reason it is employed in photography for very rapid work both on plates and films, as well as for papers and enlargements.

14. **Photography.**—Most everyone is interested more or less in photography, yet but few do much more than "press the button." In sensitizing plates and films a solution of silver nitrate and one of ammonium or potassium bromide are added to one of gelatine, whereupon the reaction shown above takes place. The emulsion is kept warm until the silver bromide has formed a fine precipitate throughout the entire mass, after which it is allowed to solidify. The mass is then cut into shreds and treated with cold water to dissolve out the ammonium nitrate which was formed as a by-product. It is then dried, melted and allowed to flow over the plate, forming a thin film. Most photographic papers used by amateurs are made in a similar way and contain the silver bromide in a thin film upon the paper. On exposure to light, plates and papers, containing silver bromide in the film, show no results. The plate is put into a solution of some reducing agent, more often now a coal tar product such as metol or hydroquinon, together with an alkaline salt such as sodium carbonate. The reducing agent acts upon the silver salt, decomposes it and sets the silver free. This occurs much more rapidly where the light has already *begun* the process. The operation is called developing the plate. Naturally, such portions of the landscape, or object being photographed, as reflect considerable light will affect the silver bromide the most, and upon developing will have the silver reduced most rapidly, hence will become dark. For this reason, since white objects appear upon the plate as black after development, it is spoken of as a *negative*. If the plate be allowed to remain in the developer indefinitely finally all the silver is reduced and the plate becomes black all over. To prevent this, at the proper time, known usually by the image beginning to appear upon the reverse side of

the plate, it is removed from the developer, rinsed and put quickly into a solution of sodium thiosulphate, called "hypo." This is an excellent solvent for silver chloride and bromide, so that any portions of these salts left unreduced by the developer are dissolved out and thus the reduction and darkening of the plate is stopped. This is called *fixing* the plate. The process is complete when on being held up to the light no white appears anywhere and the plate is more or less transparent. Developing is done under red light. Students of physics know that sunlight consists of three kinds of rays—light, heat and chemical rays. In a study of the spectrum it has been found that most of the heat rays are at the red end and most of the chemic at the violet end of the spectrum. Therefore, light passed through red glass or other red objects has most of the chemic rays filtered out. Hence, the sensitized plate is not affected by such light.

15. **Printing-Out Papers.**—There are two kinds of papers used in photography in making the prints. *Printing-out* papers have a film containing silver chloride which is not nearly as sensitive to light as silver bromide. They are placed in a printing frame under the negative and exposed directly to good sunlight. The image *prints out* slowly and can be seen as it appears. When the proper degree of intensity has been reached it is fixed and toned. The fixing is with hypo as already described. The toning is done with gold or platinum compounds in which small portions of these metals take the place of an equivalent amount of silver and give a richer and softer print. The "proof" which the photographer furnishes is on printing-out paper and has not been fixed or toned. Hence, it is not permanent, and exposed to light soon darkens all over.

16. **Developing Papers.**—Developing papers, such as velox, argo, and many others now largely advertised,

contain silver bromide in the film of gelatine. They are intended to be printed by artificial light and if used in daylight it must be very much subdued and the exposure of the briefest possible time. No image appears upon exposure, but it must be brought out as with plates and films by developing. This fact gives to such papers the name *developing papers.* With ordinary electric light an exposure of from ten to thirty seconds, depending upon the negative, soon learned by a little practice, is usually sufficient. The developing is in the usual way, but a stronger solution is used and the image must come up quickly and sharply; if it does not, the paper becomes stained and the picture ruined. It is quickly transferred to the fixing bath and after a few minutes to a tray of water where it must be washed thoroughly.

17. **Blue Prints.**—Blue prints, used somewhat for landscape work, but mostly by architects and engineers, are not made from silver compounds, but from iron. However, they will be considered at this time. A good grade of paper in a room with subdued light is brushed over with a solution of ferric ammonium citrate. This gives to the paper on the one side a pale-yellow color. For use it is exposed under a negative or architectural drawing to direct sunlight, since it is not very sensitive. When the proper exposure has been made, which may be known by a sort of bluish-bronze appearance, the paper is removed from the frame, and submerged in water. Wherever the sunlight has been able to pass through the negative or drawing it has reduced the ferric citrate to a ferrous salt, blue in color and not soluble in water. The water, therefore, washes out the unchanged yellow ferric citrate and leaves the blue in the paper. Hence, in an architectural drawing since the original lines are in black, in the print they will be white upon a blue background.

Blue print paper may easily be prepared by the student for his own use in the laboratory. Blue prints are so simple and so easily prepared that many attempts have been made to change them into sepia or black by the application of some reagent. Most formulas, however, in the hands of the amateur give rather indifferent and unsatisfactory results.

18. **Occurrence of Gold.**—As a rule gold occurs free in nature; in Colorado, however, it is sometimes found in combination with tellurium as gold telluride. Originally, probably, the grains or nuggets were scattered through veins of quartz found in cracks in the earth's crust. However, as erosion took place, the disintegrated particles of rock and gold have been carried down till now they are found in river beds and alluvial deposits in many places.

19. **Mining of Gold.**—The early history of every gold field is largely the same. The prospector recovers the coarser particles of gold by "panning" or "cradling." This consists in washing out by a rocking motion, usually in a stream of water, the sand and lighter particles. From the heavier particles remaining in the cradle will be obtained, by hand, the grains and nuggets of gold. When the field becomes *proved* as a valuable producer, capital comes in with dredging or hydraulic mining. In the latter, streams of water, brought from distances up in the mountains under tremendous pressure, are directed against the hillsides and other gold bearing deposits, which are thus disintegrated and washed down. The whole is made to flow through troughs or flumes over frequently recurring pockets of mercury or over copper plates amalgamated with mercury. In this way, the gold particles are caught by the mercury and at intervals the mercury is distilled and recovered for use again. In California large quantities of gold have been recovered in

this way; but from the fact that the great volume of water used has resulted in washing down over good agricultural lands immense quantities of sand and gravel, much litigation has resulted in recent years with the abandoning of such methods in many places. (Fig. 64.) Dredging is usually employed for working deposits along river beds. For the purpose, a boat of considerable size is constructed upon the land to be dredged near some river or water supply. A pond is dug large enough to contain the boat and the water turned in to fill it. A steam or

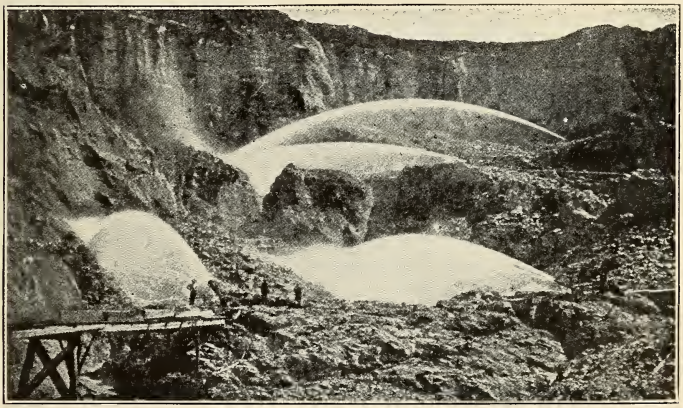


Fig. 64.—Hydraulic mining. (From Cook's "A Practical Chemistry.")

motor shovel, such as is used for extensive excavation work, is erected at one end of the boat. This scoops out the gravel in front of the vessel, swings it around upon the deck and dumps it where streams of water provided by pumps wash it off at the stern over amalgamated copper plates. The gold is caught by the mercury as already explained. Thus the pond is constantly being filled in the rear and dug out in front of the boat. Large tracts of alluvial deposits are worked in this way with very profita-

ble results. One of the best known sections in the California fields is that at Oroville. "Quartz vein mining" is the term applied to that used when tunnels are run or shafts sunk to follow the veins of gold-bearing quartz. In such cases, as the rock is brought to the surface it is sorted by hand and the portions containing little or no gold are carried by small cars to the dump and constitute the "tailings." The quartz containing the gold is crushed and the gold recovered either by the *chlorination* or the *cyanide* process. In the former, the quartz rock is roasted, which serves to bring the gold to the surface or if it be in the form of the telluride, to volatilize the tellurium and leave the gold free. It is then dissolved by liquid chlorine or by treatment with bleaching powder mixed with hydrochloric acid. From the solution of gold chloride thus obtained the metal is recovered by precipitating with ferrous sulphate or oxalic acid. If the cyanide process is used, roasting is not necessary. The gold is dissolved in a solution of potassium cyanide and precipitated from this by zinc. In many places *stamp mills* are now used. They consist of steel cylinders of considerable size and weight held upright by supports. They are continually lifted by machinery and dropped automatically upon the quartz, which is slowly fed upon the platform or table. The continued "stamping" crushes the rock into fine particles; a stream of water washes it over amalgamated plates and it is recovered as in the case of dredging.

20. **Characteristics of Gold.**—Gold is a soft, yellow metal with a specific gravity of 19 and melting point about 1,060° C. It is thus between that of silver and copper. It is the most malleable of all metals and in the form of gold leaf is beaten so thin that it is said 1,500 sheets together are no thicker than an ordinary sheet of writing paper. Gold is the least active chemically of

the more familiar metals. It is not attacked by oxygen or tarnished by hydrogen sulphide in the air as is silver. It is soluble in aqua regia in which it forms gold chloride, $AuCl_3$. It is also soluble in potassium cyanide by which a complex potassium auric cyanide is produced, $KCN.Au(CN)_3$. Nothing need be said regarding the uses of gold. When pure it is spoken of as twenty-four carats fine. Ordinary jewelry is not over fourteen carats and may even run as low as ten without being objectionable. Gold plating, or gilding, uses a cyanide solution and the process is similar to that already described for copper and silver. American gold coins are 90 per cent gold and 10 per cent copper.

**Exercises for Review**

1. Name the metals of the copper group and state their position in the periodic table. What is meant by a long period in the table?

2. What is a noble metal?

3. Describe the deposits of copper in the north; in the west. Name some important ores and give composition.

4. Give the characteristics of copper.

5. Name the most important uses of copper and state why so used in each case.

6. Name three alloys of copper and give composition.

7. Give formula for blue vitriol and state how made.

8. Explain how an electrotype is made. What advantage is there in an electrotype? Give uses for them. What is electrolytic copper? How made?

9. Name some other compounds of copper with formulas.

10. What is the source of most of our silver?

11. Give chief characteristics of silver.

12. Name some familiar uses for silver. How are mirrors made?

13. How is silver nitrate made? What is its commercial name?

14. Give characteristics of silver nitrate. Also its chief uses and state the principle underlying each use.

15. How is silver chloride made? Use?

16. How is silver bromide made? What use has it?

17. How are photographic plates and films made?

18. What is a negative? Why so called?

19. Explain the process of developing a plate.

20. Name two kinds of photographic papers. What is the difference between them in action and composition?

21. Give process of making a print on each kind of paper.

22. In what does fixing a negative consist? What reagent is used for doing this?

23. What is the sensitizing agent in blue print papers? What happens when they are exposed to the light? What does the water do?

24. What can you say of the occurrence of gold?

25. What is meant by panning? By hydraulic mining?

26. Describe dredge boat mining. How is the gold recovered? What becomes of the mercury?

27. Of what does the chlorination process consist?

28. Give the chief characteristics of gold.

29. What are the two best solvents of gold?

30. How is an article gold plated?

31. What is meant by gold eighteen carats fine?

32. What is the carat of the five dollar gold coin?

# CHAPTER XXXI

## THE MAGNESIUM FAMILY

**Outline—**

Members of the Group
Magnesium
- (*a*) Natural compounds
- (*b*) Characteristics of
- (*c*) Uses
- (*d*) The Oxide
- (*e*) Other Compounds

Zinc
- (*a*) Ores of
- (*b*) Reduction
- (*c*) Characteristics of Zinc
- (*d*) Uses
- (*e*) Zinc Sulphate
- (*f*) Zinc Chloride
- (*g*) Zinc Oxide

Mercury
- (*a*) Occurrence
- (*b*) Characteristics
- (*c*) Uses
- (*d*) Mercuric Oxide
- (*e*) The Chlorides
- (*f*) Vermilion

1. **General Comparison.**—Besides magnesium, beryllium, also known as glucinum, zinc, cadmium and mercury belong to this group. Beryllium is the lightest with an atomic weight of 9.1 and mercury the heaviest with a weight of 200. They all form compounds with a valence of two, and with the exception of mercury form no other series. Magnesium in some of its reactions resembles calcium and in analytic separations is often classed in that group.

2. **Natural Compounds of Magnesium.**—Besides the sulphate found in sea water and in springs, known as Epsom salt, magnesium chloride, $MgCl_2$, is found associated with common salt, and the double carbonate of magnesium and calcium, known as dolomite, occurs with limestone. Magnesium also is found in several natural silicates of more or less complex composition. One of the best known of these is meerschaum. It is a soft, white mineral used in making pipes for which it is prized because of the brown colors it assumes. Much more valuable than this is asbestos, a greenish, anhydrous silicate.

This mineral has a silken luster and is fibrous, so that by mechanical process it may be worked into a loose mass. In this form it has numerous uses. Mixed with magnesium oxide it is employed as an insulating material for steam pipes to prevent loss of heat by radiation; railway locomotives are thus jacketed; it is used for insulation against fire in many ways; for large stage drop curtains; in stoves; about furnaces and furnace pipes; in gaskets for steam pipe fittings; brake linings for motor cars; as a cement for expensive stucco work; imitation tile and shingle roofing and in scores of other ways.

3. **Characteristics of Magnesium.**—Magnesium is prepared much as is calcium, that is, by the electrolysis of the double salt of magnesium and potassium, $KCl.MgCl_2$. It is a grayish white metal, with a specific gravity of 1.75. In the air it reacts slowly with oxygen by which a thin coating upon the surface is formed. When heated it burns vigorously with a brilliant white light. It is one of very few elements which combines directly with nitrogen. When burned in the air an appreciable amount of the product formed is magnesium

nitride, $Mg_3N_2$. Magnesium does not react with cold water, but will set free hydrogen from boiling hot water. It is high in the electromotive series of metals and rapidly decomposes even dilute acids with evolution of hydrogen. It is brittle, but when heated somewhat it may be drawn into wires; flattened, this is spoken of as magnesium ribbon. It is also sold in the form of powder.

4. **Uses of Magnesium.**—The powdered magnesium is used extensively for flashlight work in photography. For this purpose, sometimes it is blown into the flame of a specially constructed alcohol lamp; again it is mixed with potassium chlorate, which causes a very rapid combustion of the whole mass. The same mixture is used in fireworks to give the intensely white lights in the varicolored bombs. Flashlight powders must be regarded as explosives and handled with great care. Magnalium is an alloy of magnesium and aluminum, light and tenacious in properties, at present being made for use in air ships and for similar work where a light metal is needed.

5. **Magnesium Oxide, MgO.**—This is sold under the name of magnesia. It is a fine, white powder, made by calcining magnesium carbonate, as lime is prepared from limestone. The reaction is the same,

$$MgCO_3 \rightarrow MgO + CO_2.$$

It is an excellent insulating material against loss of heat. Hence, as stated elsewhere, it is mixed with asbestos, about four parts to one, as a covering for steam pipes and all similar places where loss of heat is to be prevented. Our great railway locomotives, in cold weather, would never be able to make sufficient steam to pull a loaded train were it not for the heavy jacketing of the boilers with magnesia. Likewise, in refrigeration systems, the pipes which transmit the brine from the

source to points of use are protected against access of outside heat. For a similar reason, and because it is infusible, it is used in lining electric furnaces and for making crucibles where great heat is to be employed.

6. **Other Compounds.**—Magnesium sulphate, sold under the name of Epsom salt, is a light crystalline solid, with the formula $MgSO_4.7H_2O$. It is somewhat efflorescent. The use of the salt in medicine as a purgative is well known. It is also sometimes used in weighting cotton goods. Magnesium carbonate as prepared in the laboratory is a basic salt, having the formula $MgCO_3.Mg(HO)_2$. This is because of the hydrolysis which takes place. It is a fine, white powder often used in tooth pastes and in metal polishes. The chloride, $MgCl_2$, has been mentioned as a deliquescent salt, found in sea water, causing the dampness often observed in table salt.

7. **Occurrence of Zinc.**—The greater portion of the supply of zinc in the United States is obtained from the Joplin district, which includes not only southwest Missouri, but southeast Kansas and northeast Oklahoma. It occurs in this section as a sulphide, ZnS, known locally by the name of "jack" but scientifically as sphalerite or zinc blende. In some parts of the district it is mixed with a lead ore, galena, also a sulphide. In several of the Western States, for example, Colorado and Montana, zinc occurs mixed with copper and silver ores, usually as a sulphide; in some of the Eastern States it occurs as *franklinite,* $ZnO.Fe_2O_3$.

8. **Reduction of Zinc Ores.**—Several of the metals thus far studied, notably the silver group, are either found free or may be reduced by heat alone. Some of the copper ores, because of their complexity and mixture of other metals, require special treatment, but even

many of these may be reduced by heat alone. Most of the other metals studied thus far are reduced electrolytically. Zinc introduces a third type, those which require the aid of some reducing agent, such as carbon. The process will be considered very briefly. As carbon, even when heated, does not combine readily with sulphur, it becomes necessary to convert the zinc ores into an oxide. This is done by a process known technically as "roasting." The term means heating strongly with a plentiful supply of air. By this process the sulphur and zinc both are converted into oxides, thus,

$$2ZnS + 3O_2 \rightarrow 2SO_2 + 2ZnO.$$

The zinc oxide is next mixed with coke, heated strongly in cylindrical retorts made of fire clay. The zinc distils out in the form of vapor and is condensed.

9. **Characteristics of Zinc.**—Zinc is a bluish-white metal with a melting point of about 420° C., and boiling point of 950° C. It will be seen that a temperature sufficient to melt silver will vaporize zinc. "Spelter," as the product from the zinc smelters is called, is brittle; but if heated, at a temperature between 125° and 150° C., it becomes malleable. Rolled into sheets at this temperature its malleability becomes permanent. It is a poor conductor of heat and electricity. It is only slightly attacked by the air, for the basic carbonate which forms upon the surface is closely adhering and protects the metal almost as if painted. Water is not decomposed by zinc, but dilute acids are readily, with the evolution of hydrogen. This is especially true of commercial zinc which is somewhat impure. Molten zinc mixes readily with silver, copper, tin and antimony, but not with lead or bismuth. Melted with lead it will float as ether upon water with only a small quantity of each dissolved in the other. This fact is employed

in separating silver from lead when obtained from argentiferous lead ores.

10. **Uses.**—Because of its nonconductivity it is often used for lining refrigerators and beneath or behind stoves to protect the floors or walls. Its most extensive use, probably, is for "galvanizing" iron. This is not done electrolytically as the name might imply, but by dipping the heated iron, previously well cleaned, into molten zinc. Upon withdrawing the iron a coating of zinc adheres. Practically all iron wire fencing is now made in this way. Galvanized sheet iron is used for gutters, downspouts, cornice work, granaries, wind mills, feed and watering troughs, as well as for countless smaller articles. Dry cells consist of a container made of zinc which serves as the positive plate, a carbon rod at the center as the negative, and a packing, in part, of sal ammoniac or some other salt which reacts with the zinc. Many valuable alloys of zinc are familiar. Brass and German silver have already been mentioned. Some "white" metals, from which various articles of plated silverware are made, are an alloy of copper and zinc in which the proportion of zinc is high, to such an extent that the color of the copper is not apparent at all.

11. **Zinc Sulphate, $ZnSO_4.7H_2O$.**—Commercially this compound is known under the name of *white vitriol.* It contains the same quantity of combined water per molecule as magnesium sulphate. It may be prepared by treating zinc with dilute sulphuric acid or from the native blende in a similar manner. Like magnesium sulphate it is efflorescent. It is used somewhat as a *mordant* and to some extent as an antiseptic in medicine. A mordant is a reagent which has the power of fixing a dye in the fibers of a cloth so that it is not easily removed by water.

12. **Zinc Chloride, $ZnCl_2$.**—This is a white compound which may be prepared by treating zinc with dilute hydrochloric acid in slight excess and boiling to dryness. It is very deliquescent and in solution gives an acid reaction owing to partial hydrolysis. For this reason it is commonly used in soldering as a flux to give a clean surface. The free hydrochloric acid in the solution dissolves the film of oxide always present, so that the melted solder may come into direct contact with the metal. Melted zinc chloride has the remarkable property of being able to dissolve cellulose; by dipping sheets of paper into the liquid, parchment is made.

13. **Zinc Oxide, ZnO.**—As usually obtained, zinc oxide is a faintly yellow compound. Perfectly pure it is white when cold, but distinctly yellow when hot. It is a valuable by-product of many smelters, being obtained by the roasting of ores containing a very small percentage of zinc. The oxide is vaporized and carried over with the sulphur dioxide and other gases and is condensed in large, cool chambers upon coarse sacking. Afterward it is purified by continued heating below its point of vaporization. It is used extensively in the manufacture of paints and enamels. Ground in oil the former is sold under the trade name of "zinc white." Small quantities of the oxide, carefully purified, are used in pharmacy for making salves and other applications for skin diseases. Its action is probably largely antiseptic. It is also used in dentistry in making temporary fillings for teeth, especially for children. For this purpose it is mixed with glacial phosphoric acid (p. 280) to form a soft mass which is placed in the prepared cavity. It very soon hardens much as does plaster of Paris, forming an oxyphosphate of zinc. This oxide is of interest for the reason that it possesses a dual character, serv-

ing sometimes as if basic and again as if acidic. In the hydrated form, $Zn(HO)_2$, it readily dissolves in dilute acids, forming zinc salts, in which zinc is the positive ion. On the other hand, it will dissolve, though somewhat less readily, in strong bases, such as sodium hydroxide. It then forms salts called "zincates" in which zinc is found in the negative ion. Thus,

$$2HCl + Zn(HO)_2 \rightarrow ZnCl_2 + 2H_2O,$$
$$2NaHO + Zn(HO)_2 \rightarrow Na_2ZnO_2 + 2H_2O.$$

In these cases the zinc hydroxide evidently has ionized as follows,

$$Zn(HO)_2 \leftrightarrows H_2ZnO_2 \rightleftarrows \overset{++}{Zn} + (\overset{-}{HO})(\overset{-}{HO}) + \overset{+}{H}\overset{+}{H} + \overset{-}{Z}n\overset{-}{O}_2.$$

Therefore, although zinc hydroxide is but slightly soluble in water, such portions as do dissolve are evidently ionized in both ways in fixed definite amounts. From the location of zinc in the periodic table, not far from the diagonal, such behavior might be expected.

14. **Occurrence of Mercury.**—Mercury has been known at least since 300 B.C. when it was prepared by Theophrastus, who gave it the name meaning *liquid silver*. Its symbol is derived from the Greek word, *hydrargyrum*. It is found in comparatively small quantities and in few places in the world. In America the mines in central California are the most productive. In Europe, Spain and Austria produce the greater part. In all cases the sulphide, HgS, known as *cinnabar*, with some intermingled free mercury, is the ore found. From this the mercury is obtained by distillation.

15. **Characteristics of Mercury.**—Mercury is the only metal, liquid at ordinary temperatures. It becomes a solid at about −39° C. and boils about 360°. In the solid form mercury is somewhat malleable and to a considerable extent resembles lead. It dissolves or alloys

readily with many of the other metals, especially gold, silver, copper, tin and zinc. Such alloys are called amalgams. They may be obtained by putting the finely divided metals into mercury, or a surface amalgamation may be had by dipping the clean metal into a solution of some salt of mercury. A bit of clean gold dropped upon mercury will sink and dissolve as a lump of sugar in a cup of hot water. Again, a clean penny in a solution of mercuric nitrate soon takes on a coating of mercury which upon slight rubbing has the appearance of burnished silver. In the latter case an amount of copper has dissolved equivalent to the mercury deposited, that is, one atomic weight of copper has been dissolved for each atomic weight of mercury deposited. Mercury is not tarnished by the air, nor does it set free hydrogen from acids It decomposes nitric acid and boiling sulphuric with the usual results in such cases. The two equations following indicate the reactions,

$$3Hg + 8HNO_3 \rightarrow 3Hg(NO_3)_2 + 4H_2O + 2NO,$$
$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + 2H_2O + SO_2.$$

16. **Uses of Mercury.**—The use of mercury for amalgamating copper plates and otherwise in obtaining gold has been described. (See p. 374.) It is used in thermometers and to some extent in barometers, although the aneroid is taking the place of the mercurial barometer in many places. The advantages of mercury in thermometers are that it has a high and uniform rate of expansion through a long range of temperature and is of high boiling point. Alcohol thermometers are valuable for use below the freezing point of mercury. Zinc plates in galvanic batteries are commonly amalgamated to prevent local circuits with rapid wasting of the metal. In dentistry amalgam fillings, consisting of silver and tin with sufficient mercury to form a soft pliable mass,

are commonly used except for front teeth. This amalgam has the property of setting rapidly and of retaining its color, while dental amalgams containing cadmium, a metal formerly used considerably, turn dark and become unsightly.

17. **Mercuric Oxide, HgO.**—This is a heavy solid, crystalline or amorphous, yellow, orange or red in color, according to the method by which it is obtained. The yellow is obtained by treating a warm solution of mercuric chloride or of some other mercuric salt with sodium or potassium hydroxide solution, in slight excess. The hydroxide, formed at first, quickly decomposes into mercuric oxide and water, thus,

$$HgCl_2 + 2KHO \rightarrow Hg(HO)_2 + 2KCl \rightarrow HgO + H_2O + 2KCl.$$

It is regarded as the same chemically as the orange or red variety but in a finer state of division, since by trituration the red variety changes to yellow. It is used somewhat in medicine in the form of salves, mainly on account of its antiseptic properties.

18. **Mercurous Chloride or Calomel, $Hg_2Cl_2$.**—This is a finely divided white powder used in medicine. It is easily prepared in the laboratory by treating a solution of mercurous nitrate with a solution of common salt or hydrochloric acid, thus,

$$Hg_2(NO_3)_2 + 2NaCl \rightarrow Hg_2Cl_2 + 2NaNO_3.$$

As it is insoluble in water it is easily separated by filtration. On a large scale it is made by mixing common salt, mercury and mercuric sulphate intimately and distilling. The calomel passes over as a vapor and is condensed. It is apt to contain small quantities of the mercuric chloride and should be freed from it by washing. Like all salts of mercury, calomel is poisonous and all the excretory organs are thereby stimulated by its pres-

ence. Being an unsaturated compound it tends to take up an additional negative ion and form the mercuric salt. Therein lies the danger of its use in medicine, that of causing mercurial poisoning with consequent *salivation*. With the hydrochloric acid present in the stomach or in the presence of acid foods, the mercurous molecule begins to change into the mercuric chloride which is much more soluble. Its action then upon the system is rapid, and before it is eliminated the salivary glands may be affected, followed by the well-known soreness of gums and teeth. Such instances are not common now, for physicians, knowing the danger, administer the calomel mixed with common soda. This neutralizes the acid in the stomach and prevents the calomel changing to the soluble form. Even as given now, however, acid foods should not be used at the same time.

19. **Mercuric Chloride, $HgCl_2$.**—This is commonly known as corrosive sublimate. It is prepared by sublimating a mixture of common salt and mercuric sulphate. It is highly poisonous. The white of eggs is regarded as the best antidote, with which the mercuric salt forms an insoluble mass. Owing to its poisonous properties it is an excellent antiseptic and is frequently used for sterilizing surgical instruments and upon bandages for wounds. Applied in this way it is not poisonous. To prevent "scab," a disease which causes a rough surface upon potatoes, a dilute solution of corrosive sublimate is sometimes used in which the seed potatoes are immersed a short time before planting.

20. **Mercuric Sulphide, HgS.**—The artificial sulphide is sold under the name *vermilion*. It is a brilliant red powder, used as a pigment. Prepared in the laboratory by adding hydrogen sulphide to a solution of some mercuric salt it is a black powder. The reaction is

$$HgCl_2 + H_2S \rightarrow HgS + 2HCl.$$

If this black precipitate is sublimed, it changes to the red variety.

### Exercises for Review

1. Name the metals of the magnesium group. Where are they located in the table? What is their valence?

2. Give the important natural compounds of magnesium. What are the chief uses for asbestos?

3. Give the characteristics of magnesium. In what two forms does it occur?

4. What are the principal uses of magnesium? State why so used.

5. What is magnesia? What are its chief uses?

6. Give formulas and uses for the sulphate and carbonate of magnesium.

7. Name the important ores of zinc. Where is it mostly obtained in the United States?

8. How is zinc blende reduced? Name two other methods of reduction and some metal obtained each way.

9. Give the most important characteristics of zinc.

10. What is galvanized iron? Its important uses?

11. How is zinc sulphate obtained? Its commercial name? What other vitriols have been studied?

12. What is a mordant?

13. Give method of making zinc chloride. Name some important use.

14. What is the source of the commercial supply of zinc oxide? What is its chief use?

15. From what are the temporary fillings for teeth made?

16. Chemically, what point of interest attaches to zinc oxide?

17. Why will zinc oxide dissolve both in acids and bases?

18. What is the only ore of mercury? Where found?

19. Give the important properties of mercury. What is an amalgam? How may amalgams be made? Name some uses for them.

20. Give some valuable uses for mercury.

21. How may yellow mercuric oxide be obtained? What other varieties occur? Wherein are they different?

22. What is calomel? What danger attaches to its use as a medicine?

23. What is corrosive sublimate? Why so called? What uses has it?

24. How may vermilion be made? Of what use is it?

25. Complete these equations and state what process is represented,

$Mg + O_2 \longrightarrow$ ,
$MgCO_3$ (heated) $\longrightarrow$ ,
$ZnO + C \longrightarrow$ ,
$Zn + HCl \longrightarrow$ ,
$ZnO + HCl \longrightarrow$ ,
$HgS + O_2 \longrightarrow$ ,
$Hg_2(NO_3)_2 + NaCl \longrightarrow$ ,
$HgSO_4 + NaCl + Hg \longrightarrow$ ,
$HgSO_4 + NaCl \longrightarrow$ ,
$Hg(NO_3)_2 + H_2S \longrightarrow$ .

*Note.*—In the above equations the student must supply coefficients as needed for proper quantity of each reagent.

# CHAPTER XXXII

## THE ALUMINUM FAMILY

**Outline—**

Members of the Group
Compounds of Boron
Aluminum
- (*a*) Occurrence in Nature
- (*b*) Precious Stones
- (*c*) Manufacture of Aluminum
- (*d*) Characteristics
- (*e*) Uses
- (*f*) Alloys
- (*g*) Alums
- (*h*) Aluminum Hydroxide

1. **Members of the Group.**—Aluminum is the only important metal of the family. Boron is a member and the lightest with an atomic weight of only 11. It forms two compounds of some importance, borax and boric acid. The former has been studied under the sodium compounds. Boric acid is a white, crystalline solid, mildly antiseptic, and frequently used in solution as an eye wash.

2. **Abundance of Aluminum.**—By referring to Fig. 9 on p. 52 it will be seen that aluminum constitutes about 8 per cent of all the matter of the earth, and ranks next to silicon in abundance. It is a constituent of all clays and of the feldspar rocks from which clays are derived by decomposition. Mica, a rock which easily splits into thin leaves used in stoves and for insulation in various ways, is a silicate of aluminum and potassium. Kaolin, Fuller's earth, garnets, sapphires, emeralds, rubies, are all aluminum compounds.

Corundum, an impure oxide of aluminum, ranks next to the diamond in the scale of hardness. Emery is of the same composition and is familiar to all. It is used in various forms as an abrasive: emery powder, grindstones, and emery wheels, whetstones, emery paper and emery cloth. Kaolin is a pure white clay used in making porcelain ware and the various grades of china. Fuller's earth is a similar compound used in absorbing the coloring matter from vegetable oils such as that made from cotton seed. It also has various other uses.

3. **The Precious Stones.**—To the mineralogist, rubies, sapphires and emeralds are all *sapphires*. They are crystallized aluminum oxide, $Al_2O_3$, and differ from emery in that it is uncrystallized and less pure. Their color is due to small quantities of another metallic oxide. At the present time great quantities of these jewels are being manufactured even more perfect than the natural stones and with all their characteristics. The white sapphire, which resembles the diamond somewhat though less brilliant, is of the same composition as the other sapphires, but uncolored. These stones are sometimes spoken of as *synthetic*. For some years, it is said, over nine million carats of rubies and about half as many sapphires have been made annually. The garnet is more complex in composition than the above stones being an orthosilicate of aluminum and calcium, $Ca_3Al_2(SiO_4)_3$.

4. **Preparation of Aluminum.**—At the present time aluminum is made by the electrolysis of bauxite, a hydrated oxide of aluminum. The principle is the same as used for sodium, calcium and several other metals already studied. Bauxite, however, does not melt easily, neither does it dissolve in water. The problem, therefore, is to secure it in liquid form so that it may become a conductor. Another compound of aluminum known as cryolite, a word

which means *ice stone*, and given to this mineral because of its low melting point, is put into an electric furnace and melted. Powdered bauxite is added and dissolves readily. It will be seen that the cryolite is simply a solvent or, as it is technically called, a flux. When the current is passed the bauxite decomposes and the aluminum collects at the cathode. Fig. 65 illustrates the process. Fresh quantities of bauxite are added from time to time as needed, the aluminum is drawn off occasionally and the process is continuous. The heat generated by the resistance to the current keeps the cryolite melted. The manufacture of aluminum is carried on where cheap

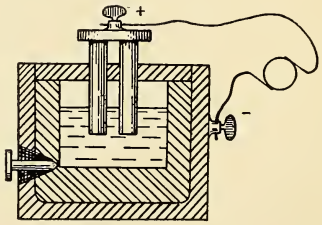



Fig. 65.—Manufacture of aluminum.

electric power may be had, especially at Niagara Falls. Up to the present time no commercial method has been devised for extracting aluminum from such complicated compounds as clays. Such a process would be eminently desirable.

5. **Characteristics of Aluminum.**—Aluminum is a white metal, of low specific gravity, being only 2.6 times as heavy as water. It is an excellent conductor both of heat and electricity. As a given weight of aluminum will make a wire of much greater cross section than the same weight of copper, it is even better than copper as a conductor. In tensile strength it is not greatly different from copper and most other common metals, ex-

cept steel, but it has a tendency to crystallize and unprotected wires to become somewhat brittle. Its melting point is about 700° C. At ordinary temperatures it does not react appreciably with oxygen and does not tarnish greatly in the air. It is ductile and malleable and easily made into thin foil. While it is below magnesium in the electromotive series of metals, it is strongly positive. It decomposes concentrated hydrochloric acid vigorously, with the evolution of hydrogen. With nitric acid the action is practically *nil;* with sulphuric acid there is

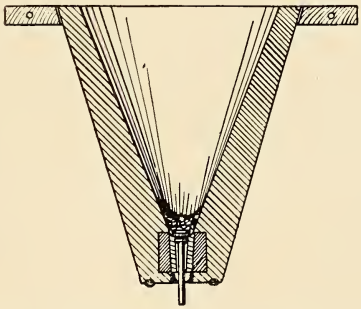


Fig. 66.—Thermit crucible, sectional view.

practically no action at room temperature, but when heated to boiling the metal is oxidized and sulphur dioxide evolved as is usual in such cases. Strong alkaline solutions attack aluminum readily and form a class of salts called *aluminates*, corresponding to the zincates, mentioned previously.

6. **Uses.**—On account of its electric conductivity it is used in some localities as feed wires for trolley systems. In the home it makes an ideal cooking vessel. Its conductivity is about the equal of copper, so that all portions of the vessel become heated alike and food products which burn easily are much less readily scorched

than in ordinary granite ware or tinware. Further, it is not attacked by weak acids such as those found in any fruits used as food. Moreover, it is light, does not tarnish readily, and is easily cleaned. Anything alkaline

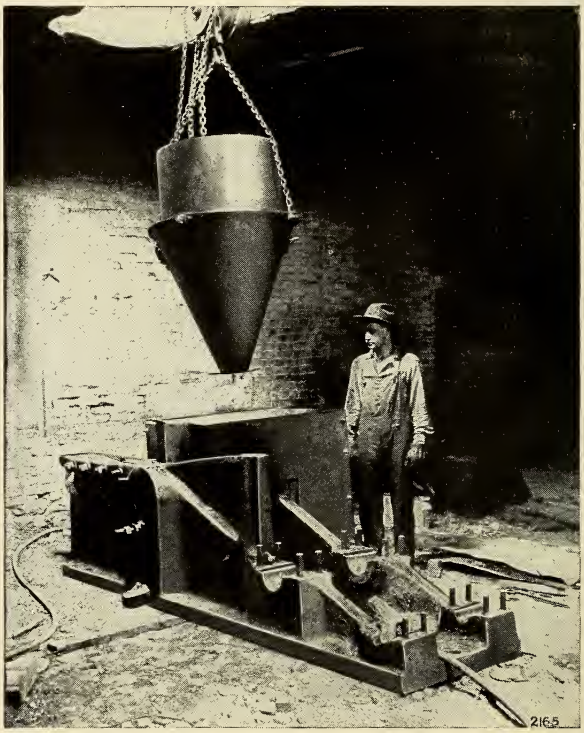



Fig. 67.—A thermit crucible ready for use in mending a broken casting. (By courtesy of the Goldschmidt Thermit Co.)

in character cannot be cooked in aluminum vessels but none of our food is alkaline. In the finely powdered form aluminum is mixed with linseed oil and used as a paint for metallic objects to which it adheres well. Its use in this way is seen in many of the penny-weighing

machines, mail boxes, steam and hot water radiators, and other familiar objects. Very considerable quantities of powdered aluminum are used in a patented article called "thermit." This consists of ferric oxide and

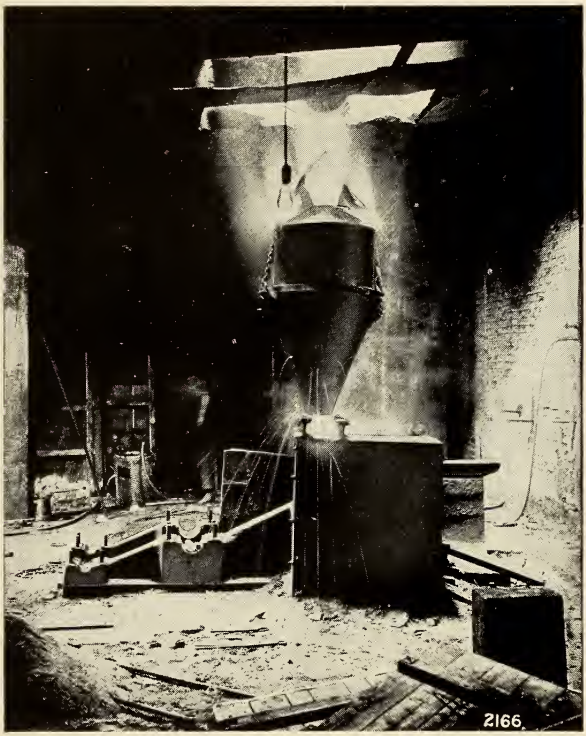



Fig. 68.—A thermit crucible in operation, mending a broken casting. (By courtesy of the Goldschmidt Thermit Co.)

aluminum intimately mixed; for use it is put into a crucible of suitable size, conical in shape, as shown in Fig. 66, and a small amount of powdered magnesium placed on top as kindling. When everything is ready the magnesium is lighted. The heat thus obtained is sufficient

to *start* the chemical action between the aluminum and ferric oxide, $Fe_2O_3$. Once begun it is self continuous from the heat liberated. In a short time the aluminum has become aluminum oxide and the iron is free, in a molten condition with a temperature over 1,500°. In fact, it is said that a temperature of 3,000° is often reached in the process. By substituting the oxides of other metals, such as chromium or vanadium or manganese, it is possible to obtain these rare metals in a pure condition. The process is used for welding almost everything of any size, made of iron or steel. Thus are mended broken drive wheels for locomotives, propeller shafts for great engines, rails in street railway systems, and the like. It is frequently used on shipboard for repairs not easily made otherwise. The aluminum oxide obtained as a by-product, is often used for the manufacture of synthetic rubies and sapphires already mentioned and as an abrasive. Another extensive use for aluminum is in the manufacture of steel. There is a tendency for molten steel, made as much of it is, to retain oxygen or other gases within the mass. This is probably due to the viscosity. When such ingots of steel are made into rails these "air holes" form weak places and probably are occasionally the cause of railway accidents. On account of the tendency of aluminum to combine with oxygen readily at high temperatures, a certain amount of the metal is added to the steel: the aluminum combines with the oxygen, forms a kind of slag and rises to the top.

7. **Alloys.**—Aluminum forms several alloys of value. Magnalium, containing about 2 per cent of magnesium, has already been mentioned. (See p. 381.) Aluminum bronze is prepared in two varieties, one with a very small percentage of copper, which is even whiter than pure aluminum and resembles silver closely except in

density. It is used extensively in novelty articles and occasionally in such kitchen utensils as teapots. The other variety, with copper as high as 90 per cent, somewhat resembles gold in color and is frequently used in making watch cases as well as a great variety of novelty articles.

8. **Alums.**—An alum is a double sulphate of a univalent and a trivalent metal. There are many of them, but the most common is potassium aluminum sulphate, $K_2SO_4.Al_2(SO_4)_3.24H_2O$. Almost as common is ammonium alum in which ammonium has taken the place of the potassium in common alum. Sodium being univalent, enters into the composition of several alums; chromium and trivalent iron, likewise, may take the place of aluminum in common alum. They are all hydrates and contain the same amount of water; they are all also *isomorphous*, that is, they all crystallize in the same shape. "Burnt" alum is obtained by heating alum to expel the water of combination. It is a mild caustic and is sometimes used medicinally in that way, especially for ulcerations of the mouth.

9. **Uses of Alum.**—Mention has already been made that alum is used as a coagulant in purifying muddy waters for city supplies. More often, not alum, but aluminum sulphate is used, although it is generally referred to as alum. Its reaction with the milk of lime is

$$3Ca(HO)_2 + Al_2(SO_4)_3 \rightarrow Al_2(HO)_6 + 3CaSO_4.$$

Likewise, alum has been spoken of as an ingredient of baking powders. More often, here also, aluminum sulphate is used instead of real alum. It is supplied the baking powder factories under the trade name of C.T.S. meaning "cream tartar substitute." The chemical action has already been noted on page 329.

10. **Aluminum Hydroxide, $Al_2(HO)_6$.**—This is easily

prepared in the laboratory by treating a solution of alum with ammonium or sodium hydroxide, taking care not to use the latter reagent in excess. Sodium carbonate may be substituted for the alkali. It is a white gelatinous precipitate, in many ways a very interesting compound chemically. Like zinc hydroxide, it ionizes both as a base and as an acid, thus.

$$Al(HO)_3 \rightleftarrows \overset{+++}{Al} + (\overset{-}{HO}),\ (\overset{-}{HO}),\ (\overset{-}{HO}),$$
$$H_3AlO_3 \rightleftarrows \overset{+}{H},\ \overset{+}{H},\ \overset{+}{H} + \overset{---}{AlO_3}.$$

As a result aluminum hydroxide is very soluble not only in acids, with which it forms aluminum salts with aluminum as the positive ion, but is also soluble in bases, with which it forms *aluminates,* in which the negative ion is $-AlO_3$. To illustrate,

$$Al(HO)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O,$$
$$H_3AlO_3 + 3NaHO \rightarrow Na_3AlO_3 + 3H_2O.$$

Its position in the table, near the acid forming elements, would lead us to expect such behavior.

On account of its gelatinous character not only has it the power of clarifying muddy waters, but also of removing colors from solutions. Thus, if an alum solution, deeply colored with some dye, such as carmine, has a little alkali added to precipitate the aluminum as hydroxide, in settling, the aluminum hydroxide will carry with it practically all the coloring matter. Such precipitates dried and ground in oil are sold as tube paints for artists under the name of *lakes,* of crimson and other brilliant colors. It is the same principle that makes it a good mordant. Precipitated within the fibers of the cloth it holds or fixes the color. Canvas for tents and other fabrics are sometimes waterproofed by this compound. Treated first with aluminum chloride or some similar compound

the cloth is heated by steam which hydrolyzes the aluminum compound, forming aluminum hydroxide within fibers of the cloth. Upon drying it becomes waterproof. Some papers are *sized* by aluminum hydroxide. To the pulp aluminum sulphate and rosin soap are added; through hydrolysis aluminum hydroxide is precipitated in the pulp. When dry it is run between hot rollers. This melts the rosin and gives a surface to the paper while the aluminum hydroxide fills the pores, so that ink is not taken up readily.

### Exercises for Review

1. Name the members of the aluminum family and give location in the table.
2. State what is true of the abundance of aluminum. Name some familiar natural compounds.
3. What is emery? The ruby? Kaolin? A synthetic stone?
4. Describe the preparation of aluminum. What is a flux?
5. Give the characteristics of aluminum.
6. Why is aluminum suited for cooking vessels? What advantage has it over copper?
7. Describe the use of thermit.
8. Name some alloys of aluminum and give uses.
9. What is an alum? Name two. What is burnt alum?
10. What is the meaning of the term isomorphous?
11. Why is aluminum hydroxide soluble in both acids and bases? What other hydroxide has been seen to have the same property?
12. How are painters' lakes made?
13. What is meant by sizing paper?
14. Complete the following equations,

$Al_2(SO_4)_3 + KHO \rightarrow$ ,
$Al_2(HO)_6 + H_2SO_4 \rightarrow$ ,
$Al_2(HO)_6$ (heated) $\rightarrow$ ,
$Al_2O_3$ (electrolyzed) $\rightarrow$ ,
$Fe_2O_3 + Al \rightarrow$ ,
$Al + O_2 \rightarrow$ .

*Note.*—The student will use the amounts as needed in the above equations.

# CHAPTER XXXIII

## THE LEAD FAMILY

**Outline—**

- Members of the Group
- Tin
  - (*a*) Occurrence
  - (*b*) Characteristics
  - (*c*) Uses
  - (*d*) Alloys
  - (*e*) Compounds
- Lead
  - (*a*) Occurrence
  - (*b*) Characteristics
  - (*c*) Uses
  - (*d*) Alloys
  - (*e*) Compounds
    - (*a*) The Oxides
    - (*b*) Lead Acetate
    - (*c*) White Lead
    - (*d*) Chrome Yellow
  - Storage Batteries

1. **Metals of the Group.**—The only common metals belonging to this group are tin and lead, the former with an atomic weight of 119 and the latter, 207.1. Their position in the table should show a valence of four and their higher oxides indicate this.

2. **Occurrence of Tin.**—The oldest tin mines of the world are those of Cornwall, England. It is said that the ancient Phoenicians obtained their supplies from this source. These mines now at great depth and extending out under the ocean are still in operation but produce scarcely 10 per cent of the world's output of the present time. Most of that used comes from the

East Indies where it is found as tin oxide, $SnO_2$, called *cassiterite*. It is the same ore as that from the English mines.

3. **Characteristics.**—Tin is a white metal with a melting point of 232° C. It is soft, very malleable and has a specific gravity of 7.3. It is crystalline in structure, but much less so than antimony or bismuth. Like phosphorus, sulphur and some other elements already studied, tin also occurs in an allotropic form not often seen. Kept continuously below 20° C. it sometimes changes to a gray powder, expanding to such an extent that its specific gravity is only 5.8. Tin is not tarnished in the air or attacked by any of the organic acids. It decomposes hydrochloric acid with the evolution of hydrogen, also concentrated nitric, with the formation of nitrogen peroxide. Hot sulphuric acid gives off with tin sulphur dioxide, as is usual in such cases.

4. **Uses of Tin.**—Because of its permanence in the air tin is used extensively in protecting iron in what is called "tin plate." It is made in a manner similar to that used for galvanizing iron. Clean, heated sheets of steel are dipped into molten tin and upon removal a coating adheres. However, as iron is more electropositive than tin, if the coating is scratched so as to expose the iron the corrosion is then rapid. The reverse is true with galvanized iron. Of tin plate are made the so-called "tin cans" used so extensively in preserving various food products. During the year 1919 more than six billion tin cans were used in the United States in the various canned-food industries. In the infancy of food preservation in this manner, each canner made in his own establishment by hand labor the cans needed. A good workman could not produce over 150 per day; now by machine they are turned out at the rate of about

one per second. Heavy tin plate is used for roofing and gutters. Some years ago cooking vessels of tin plate were common, but they have been largely replaced by granite ware, which is more serviceable, and more recently by aluminum. Copper cooking vessels used in large eating houses, such as the Harvey system, are tinned on the inside to prevent attack by organic acids. This has to be done somewhat frequently, but the process is simple. The vessel is thoroughly cleaned as if for soldering, is heated to the melting point of tin and then the powdered metal rubbed on the surface to which it adheres. The flux used in cleaning the copper, usually ammonium chloride, prevents oxidation when the vessel is heated. Common brass pins usually have a thin coating of tin to prevent their tarnishing in the air.

5. **Alloys.**—Many valuable alloys of tin are used in the arts. Bronze is composed of copper and tin, sometimes with zinc added; brittania and pewter have already been mentioned, as have certain fusible alloys. (See p. 289.)

Soft solder contains tin and lead in equal proportions. Tin is also an important component of the most common dental amalgams.

6. **Compounds.**—Tin forms both stannous and stannic salts, represented by the chlorides, $SnCl_2$ and $SnCl_4$. The stannous chloride is an unsaturated compound and therefore a reducing agent. Added to a solution of mercuric chloride, first a white precipitate of calomel is obtained; upon warming or adding more stannous chloride a gray or black precipitate is formed consisting of finely divided mercury or a mixture of it with mercurous chloride. These two equations represent the reactions occurring,

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg_2Cl_2,$$
$$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + 2Hg.$$

The experiment serves as a test for mercuric compounds, or reversed, for a stannous salt. On account of this reducing power of stannous chloride it is used with gold chloride in toning printing out papers as already described.

There are two oxides of tin, stannous, SnO, and stannic, $SnO_2$. The latter is the compound found native. It may be obtained by treating tin with concentrated nitric acid and heating the white powder obtained. It is white when cold, but distinctly yellow when hot. Stannic acid, which is a white gelatinous compound, is used extensively in weighting silk goods. The chlorides are used somewhat as mordants.

7. **Occurrence of Lead.**—Galena, PbS, is the only important ore of lead. It is a lustrous, dark gray mineral crystallizing in cubes, with cubical lines of cleavage. It is associated with many of the zinc deposits in southwest Missouri and with silver and other metals in many of the Western States.

8. **Characteristics of Lead.**—Lead is a dark gray metal with a specific gravity of 11.38; it is soft and malleable but of little tenacity. It tarnishes somewhat readily in the air, but the coating adheres firmly and serves to protect the metal from further oxidation. The melting point is 325° C. Being just above hydrogen in the electromotive series it has little power of replacing that element in acids. With nitric acid it reacts as do most of the metals to form nitric oxide, thus,

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 4H_2O + 2NO.$$

Sulphuric acid, boiling hot and much concentrated produces sulphur dioxide, thus,

$$Pb + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + SO_2.$$

Acetic acid, though a weak organic acid, reacts slowly with lead, forming the acetate. Lead salts are all poisonous and are difficult of elimination from the system, hence are what are called *accumulative* poisons.

10. **Uses.**—Lead is used largely for making pipe. Molten lead near the point of solidification is forced by hydraulic pressure through annular openings. It is used as waste pipes in plumbing, and for protecting overhead and underground electric cables. In sheet form lead is used to line the rooms where chamber sulphuric acid is manufactured, also for sinks in chemical laboratories and other places where acids are used. Many of its alloys are valuable. Common solder has been mentioned as has also type metal, containing lead, antimony and tin. It will also be recalled that shot is an alloy of lead and arsenic. Alloyed with antimony it is used extensively in making storage batteries.

11. **The Oxides.**—Three oxides of lead are common, the monoxide, PbO, often called *litharge;* lead dioxide, $PbO_2$; and minium, $Pb_3O_4$, often called *red lead.* The first is of light brown color, the second dark brown and the third red. All are in the form of powders. Litharge is a by-product of the silver refineries and is used largely in the manufacture of flint glass. (See p. 300.) Red lead is used in making gas-tight joints in plumbing, also as a red paint for metals. The dioxide is used in storage batteries.

12. **Lead Acetate, $Pb(C_2H_3O_2)_2.3H_2O$.**—Commercially this is known as *sugar of lead* because of its sweet taste. It is easiest made by treating lead monoxide with acetic acid, thus,

$$PbO + 2HC_2H_3O_2 \rightarrow H_2O + Pb(C_2H_3O_2)_2.$$

It is a white crystalline salt, readily soluble in water. It is often used in solution as an external application in cases of "ivy poisoning."

13. **White Lead.**—Chemically, white lead is basic lead carbonate, $Pb(HO)_2.2PbCO_3$. It is the most commonly used white paint. It was formerly made entirely by what was known as the "old Dutch process" which required several weeks for its completion. It consisted in the exposure of "buckles" or short strips of sheet lead to the fumes of strong vinegar or acetic acid, and the introduction of carbon dioxide. This gas was obtained from tan bark which was used to cover the pots containing the lead and acid. The heat needed was obtained by the decomposition of refuse from stables with which the pile of pots was covered. At the present time most of the commercial supply is manufactured by a more rapid process. By means of compressed air with an apparatus on the order of an atomizer, the molten lead is made into a fine dust. This is treated with acetic acid, and owing to the finely divided condition of the lead, the process is completed in a few days. Carbon dioxide is then introduced or sodium carbonate added, which produces the basic carbonate. It is dried and ground in linseed oil. White lead as a paint has one disadvantage in sections where much soft coal is used. Considerable quantities of hydrogen sulphide are produced. This gas reacts with the lead compounds forming the sulphide, PbS, which is black. The paint as a result becomes grayish in color. The following equation will illustrate the interchange,

$$PbCO_3 + H_2S \rightarrow PbS + H_2O + CO_2.$$

Zinc white, the other common white paint, when thus treated does not change in color, for the reason that

zinc sulphide is a pure white compound, $ZnO + H_2S \rightarrow H_2O + ZnS$.

14. **Lead Chromate, $PbCrO_4$.**—Commercially known as *chrome yellow*, lead chromate is probably the best yellow pigment to be had. It is prepared by treating lead acetate in solution with potassium chromate or dichromate. Lead chromate is insoluble in water, hence forms a precipitate. It is filtered out, washed, and dried. For use it is ground in oil.

15. **Other Compounds.**—The chloride, $PbCl_2$, nitrate, $Pb(NO_3)_2$, and sulphate, $PbSO_4$, are three well-known compounds, but they have few practical uses and need

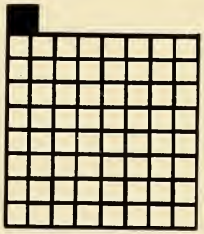


Fig. 69.—A battery "grid."

not be considered here. Lead iodide, dissolved in boiling water and allowed to cool, crystallizes out again in beautiful golden scales.

16. **Storage Batteries.**—In this day of motor cars a study of lead would hardly be complete without something about storage batteries. Each cell of a storage battery consists of a number of lead plates or "grids" separated from each other by thin sheets of wood. One set of these grids is connected to the positive post or pole and the other alternating set to the negative post. The wood serves to keep them from touching each other yet does not prevent the passage of the ions from one plate to another. These grids are not solid sheets of

lead but mere skeletons like the registers over hot-air furnace pipes as shown in Fig. 69. One set is packed tightly with lead dioxide or with red lead or both mixed: the other set with finely divided lead. They are then placed in a container with dilute sulphuric acid as the electrolyte. In charging the battery a current is led in from a dynamo during which time the lead dioxide is the anode. To this the sulphate ions will be attracted, which in combining with the lead oxide will give up their negative charge and convert a portion of the oxide into sulphate. The hydrogen ions of the sulphuric acid will move to the cathode, and, giving up their charge, the hydrogen escapes, leaving the lead plate positively charged. Two to three days are needed in bringing the battery up to the desired strength. When put into service, what was the negative pole or cathode now becomes the positive pole. The reverse process now takes place; the lead is slowly converted into sulphate as it loses its positive charge and the sulphated oxide at the other pole is slowly reduced to oxide again by the hydrogen ions which move in that direction.

### Exercises for Review

1. Name the metals of the lead group. Look up the table and see if any other elements belong in the same family.

2. What can you say of the occurrence of tin? What is the name of the only ore?

3. Describe tin. Under what conditions may the amorphous variety form?

4. What is tin plate? Give some of the uses for tin plate.

5. Give some other uses for tin. Name its more important alloys.

6. What two classes of compounds does tin form? Why is stannous chloride a reducing agent?

7. Name the oxides of tin and give formulas.

8. What is the chief ore of lead? Where found in the United States?

9. Describe lead. Where is it in the electromotive series? What does this tell one about the reaction of a metal with an acid?

10. Give the more important uses of lead.

11. How is lead pipe used? How made?

12. Name three oxides of lead and give formulas.

13. How is sugar of lead made? Write equation.

14. What is white lead? How formerly made? How made at present?

15. What is chrome yellow? What is its use?

16. Describe the construction of a storage battery.

17. What is an electrolyte? What is the electrolyte in a storage battery?

18. Why do instructions in regard to care of storage batteries tell one not to bring a lighted match near?

19. If the water in the battery did not evaporate at all, would it still be necessary to add distilled water occasionally? Explain your answer.

20. Complete the following equations using amounts as may be needed,

$$PbCl_2 + H_2SO_4 \rightarrow ,$$
$$Pb(NO_3)_2 + KI \rightarrow ,$$
$$Pb + H_2SO_4 \rightarrow ,$$
$$PbCl_2 + K_2CrO_4 \rightarrow ,$$
$$PbO + HNO_3 \rightarrow ,$$
$$Pb + HNO_3 \rightarrow ,$$
$$PbS + O_2 \rightarrow .$$

## CHAPTER XXXIV

## THE CHROMIUM FAMILY

Outline—

- Members of the Group
- Chromium
  - (*a*) Preparation
  - (*b*) Characteristics
  - (*c*) Uses
  - (*d*) Compounds
    - (*a*) Chromates
    - (*b*) Dichromates
    - (*c*) Chromic Salts
- Tungsten
- Uranium

1. **Members of the Group.**—To this group belong chromium, molybdenum, tungsten and uranium, all of them rather unfamiliar elements. Their higher oxides all show a valence of six as would be expected from their position in the table. Chromium has an atomic weight of 52, molybdenum, of 96; tungsten, 184; uranium, 238.5.

2. **Preparation of Chromium.**—The easiest method of obtaining chromium is by the thermit process in which chromic oxide is substituted for the ferric oxide. This has been described on p. 397.

3. **Characteristics of Chromium.**—Chromium is a metal of very high melting point, steel-gray in color and very hard. It does not tarnish readily in the air. With warm hydrochloric acid it reacts with the evolution of hydrogen.

4. **Uses.**—The chief use of chromium is in making an alloy with steel which is called chrome steel. It pos-

sesses unusual hardness and resistance to stress. It is used in parts of machinery as motor cars and trucks where great strength is required.

5. **Classes of Compounds.**—Chromium forms several series of compounds of interest to the chemist. The oxide, $CrO_3$, is acidic, the anhydride of chromic acid, corresponding to sulphuric acid. With the metals it forms a number of salts called chromates. One of the most common of these is potassium chromate, $K_2CrO_4$, a crystalline salt of lemon-yellow color. From the chromates by treatment with an acid, another set of salts is obtained, called the dichromates, of which potassium dichromate, $K_2Cr_2O_7$, is the most common. Its formula might be written, $K_2CrO_4.CrO_3$. Another oxide of chromium gives a series of salts in which chromium is the positive ion. Thus chromic oxide, $Cr_2O_3$, is a basic oxide with the corresponding hydroxide, $Cr_2(HO)_6$, also written $Cr(HO)_3$. Theoretically it is formed thus,

$$Cr_2O_3 + 3H_2O \rightarrow 2Cr(HO)_3.$$

If to this acids are added we obtain the corresponding salts. Chromic compounds are mostly green or violet; in fact, the word chromium is from the Greek for *color*, given because so many of the compounds of this metal are highly colored. The following equation shows the preparation of the sulphate,

$$2Cr(HO)_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6H_2O.$$

6. **Conversion of One Class to Another.**—Very readily these compounds may be changed from one class into another. Since the dichromates contain an anhydride, seen when potassium dichromate is written, $K_2CrO_4.CrO_3$, they may be regarded as acid salts. The addition of an alkali, therefore, should neutralize the anhydride and make a normal salt of it. In other words, it should

become a chromate. This actually happens as shown by the following equation,

$$K_2CrO_4.CrO_3 + 2KHO \rightarrow 2K_2CrO_4 + H_2O.$$

At the same time the color should change, as it does, from orange to lemon-yellow. On the other hand, the addition of an acid to the chromate converts it into the dichromate, thus,

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2SO_4 + H_2O + K_2CrO_4.CrO_3.$$

Chromates or dichromates treated with hydrochloric acid and, especially if a reducing agent be present, are changed into green salts with chromium as the positive ion, thus,

$$K_2Cr_2O_7 + 14HCl \rightarrow 2CrCl_3 + 7H_2O + 2KCl + 3Cl_2$$
$$2K_2CrO_4 + 3H_2S + 10HCl \rightarrow 2CrCl_3 + 8H_2O + 4KCl + 3S.$$

On the other hand, compounds containing chromium as a positive ion may be changed to chromates by heating with an alkali. Oxygen is taken up from the air, thus,

$$4Cr(HO)_3 + 8NaHO + 3O_2 \rightarrow 4Na_2CrO_4 + 10H_2O.$$

7. **Chromic Compounds.**—Most of the chromic compounds are green in color; however, chromic alum, $K_2Cr_2(SO_4)_4$, is violet. Chromic oxide, $Cr_2O_3$, is a green powder. It is used as a pigment, in coloring glass a deep green and in artificial emeralds. Chromic chloride, $CrCl_3.6H_2O$, may be prepared by treating chromium hydroxide with hydrochloric acid. It is of a bright green color. Chromium sulphate, $Cr_2(SO_4)_3.10H_2O$, is of a reddish-violet color, made by treating the hydroxide with sulphuric acid.

8. **Insoluble Chromates.**—Potassium chromate already named is readily soluble in water. If to this is added a

solution of lead acetate an insoluble compound of lead chromate precipitates out, thus,

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 \rightarrow PbCrO_4 + 2KC_2H_3O_2.$$

It has been mentioned already as a bright yellow pigment. Chrome red is a basic lead chromate with the composition, $PbO.PbCrO_4$; it is of bright red color. Silver chromate, $Ag_2CrO_4$, of deep red color and barium chromate, $BaCrO_4$, a pale yellow, are both insoluble compounds.

9. **Tungsten.**—The symbol for this element is W. Deposits of tungsten are said to exist in both South Dakota and Colorado, but most of our supply is imported. It is of interest mainly because of the fact that the filament of most electric light bulbs is now made from it. Such lamps give a much whiter and more brilliant light than the old carbon ones. For the same candle power tungsten lamps consume much less current and hence are much less expensive. When first introduced they were very fragile and required most careful handling, hence were not received favorably by the public. That objection has now been removed and their life is practically the same as that of the carbon lamp, that is about 1,000 light hours.

10. **Uranium.**—Uranium has the highest atomic weight of all the elements, 238.5. It is also remarkable in that, contrary to our general ideas of elementary matter, it has the property of disintegrating and forming other elements. Thus, one of the products of uranium is radium, and from radium by a similar decomposition, helium is obtained. So, uranium forces us to the conclusion that at least some elements are capable of self disintegration.

### Exercises for Review

1. Name the elements of the chromium group, and give symbols.
2. What is the simplest method of obtaining pure chromium?
3. Give chief properties of chromium.
4. For what is chromium used?
5. Name three classes of chromium compounds and give one example of each.
6. Name two oxides of chromium with formulas. Which one is acidic? Of what acid is it the anhydride?
7. Why will an alkali change a dichromate into a chromate? Illustrate.
8. Show how chromates may be changed into dichromates.
9. How may chromates or dichromates be changed into chromic salts?
10. Name three chromic salts and give formulas.
11. Name four insoluble chromates and give formulas; also uses, if any.
12. What use has tungsten? Why are such lamps desirable?
13. What is the most remarkable property of uranium?
14. Complete the following equations, using amounts needed to balance,

$$Cr(HO)_3 + HCl \longrightarrow ,$$
$$Cr(HO)_3 + H_2SO_4 \longrightarrow ,$$
$$Cr_2O_3 + H_2SO_4 \longrightarrow ,$$
$$CrO_3 + H_2O \longrightarrow ,$$
$$Cr_2O_3 + H_2O \longrightarrow ,$$
$$K_2CrO_4 + AgNO_3 \longrightarrow ,$$
$$K_2CrO_4 + BaCl_2 \longrightarrow ,$$
$$PbCl_2 + K_2CrO_4 \longrightarrow .$$

15. In Section 6, remembering that reduction consists in lowering the valence of an element and oxidation is the reverse, raising the valence, has chromium been oxidized or reduced in the last three equations given?
16. In the first two equations in Section 6, has chromium been oxidized or reduced? Give reason for your answer.

## CHAPTER XXXV

## MANGANESE AND COMPOUNDS

**Outline—**

Manganese
- Relation to Other Elements in the Table
- Characteristics
- Compounds
  - (*a*) The Oxides
  - (*b*) Manganic Compounds
  - (*c*) Manganates
  - (*d*) Permanganates

1. **Position in Periodic Table.**—Manganese is found in the same column in the table as the halogen group, but at the left hand side of the space. The corresponding positions in the long periods that follow manganese, by looking at the table are seen to be vacant. So at present this element is all alone.

2. **Characteristics.**—In some respects manganese resembles iron. It occurs in nature as a dioxide, $MnO_2$, called *pyrolusite*, always mixed with iron. It is a grayish metal, with the power of reacting with dilute acids and evolving hydrogen. It forms an alloy with iron and is tarnished when exposed to the air. Its chief use is in making *manganese steel*, by alloying it with iron.

3. **The Oxides.**—Manganese forms five oxides most of which are of no great importance. The lowest is MnO, which is a basic oxide; as they increase in amount of oxygen, as might be expected, they become more acidic until the highest is reached, $Mn_2O_7$, which is strongly acidic. The dioxide is the most familiar to the student because he has used it on several occasions. The hep-

toxide shows the metal to have the combining power or valence of seven as would be expected from its position in the table. We have used the dioxide catalytically in making oxygen, and as an oxidizing agent in the preparation of bromine and chlorine. It is a basic oxide and unites readily with acids to form manganous salts.

4. **Manganous Salts.**—Manganese forms both manganous and manganic salts just as chromium does, but the manganous are the more common. They may be obtained from manganese dioxide by treatment with an acid. Thus manganese dioxide with hydrochloric acid gives the chloride,

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2.$$

On evaporation the solution gives a pink crystalline hydrate, with the formula, $MnCl_2.4H_2O$. The sulphate may be obtained by treating the dioxide with sulphuric acid, thus,

$$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2.$$

It is also a pink hydrate, but the quantity of water varies at different temperatures. At ordinary conditions the formula is $MnSO_4.5H_2O$. Manganous salts or the dioxide, fused with borax, impart an amethyst color to the bead.

5. **Manganates and Permanganates.**—Manganese forms a series of salts known as manganates, of which potassium manganate, $K_2MnO_4$, is one of the more common. The permanganate, $KMnO_4$, is a much more important compound. It is a purple solid with greenish luster, and crystallizes in small rhombic prisms. In solution it gives a deep purple color. It has frequent use in the chemical laboratory in estimating the quantity

of iron and in various other ways. It is sometimes used in cisterns for oxidizing the organic impurities present.

### Exercises for Review

1. Give the location of manganese in the table.
2. How does the element occur in nature?
3. Give the chief properties of manganese.
4. What is the chief use of manganese?
5. How many oxides of manganese are there? Name two and state whether basic or acidic.
6. Describe the appearance of manganese dioxide. What uses has it?
7. How may manganous chloride be made? Describe it.
8. Describe potassium permanganate. Give its uses.
9. Complete these equations, using such amounts as are necessary,

$MnO_2 + HBr \longrightarrow$ ,
$MnO_2 + HCl \longrightarrow$ ,
$Mn_2O_7 + H_2O \longrightarrow$ ,
$Mn(HO)_2 + H_2SO_4 \longrightarrow$ ,
$MnCl_2 + KHO \longrightarrow$ ,
$MnSO_4 + Ca(HO)_2 \longrightarrow$ .

10. In the following equations, what substances have been reduced and what oxidized?

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$,
$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow 5Fe_2(O_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

# CHAPTER XXXVI

## THE IRON GROUP

**Outline—**

- Members of the Group
- Iron
  - (*a*) Occurrence
  - (*b*) Reduction of
  - (*c*) The Blast Furnace
  - (*d*) Wrought Iron
  - (*e*) Steel
    - (*a*) Cementation Process
    - (*b*) Bessemer Process
    - (*c*) Open Hearth Process
    - (*d*) Characteristics
    - (*e*) Method of Tempering
    - (*f*) Varieties of
  - General Characteristics of Iron Compounds
    - (*a*) Ferrous Sulphate
    - (*b*) Ferric Chloride
  - Oxidation and Reduction of Salts
  - Pigments
- Nickel
  - (*a*) Characteristics
  - (*b*) Uses
  - (*c*) Compounds
- Cobalt
  - (*a*) Characteristics
  - (*b*) Compounds

1. **Members of the Group.**—Iron, nickel and cobalt are usually associated, but not as a periodic group. They have atomic weights close together and do not form a vertical column in the table. Two of them are elements of importance, iron being intrinsically the most valuable of all metals.

2. **Occurrence of Iron.**—There are several ores of iron used in the preparation of the metal. Of these, hematite, $Fe_2O_3$, is the most important. It is a dark colored mineral, reddish-brown to black, which drawn across a piece of unglazed porcelain gives a dull red streak. It is this fact that gave the name to the ore, the word hematite being from the Greek meaning *blood*. Limonite, which is a hydrated oxide, $Fe_2O_3.3H_2O$, gives a yellow streak, and received its name from the Latin word for *lemon*. In some sections, the magnetic oxide, $Fe_3O_4$, is found. The carbonate, $FeCO_3$, called *siderite*, and the disulphide, $FeS_2$, commonly known as "fool's gold" should also be mentioned. Iron never occurs free upon the earth except in very minute quantities. Meteorites have been discovered containing from 92 to 97 per cent of iron and the remainder nickel. Lieutenant Peary, some years ago, in one of his Arctic trips discovered through the aid of his Esquimos two large meteorites, one of which weighed in the neighborhood of 100 tons, the largest ever found. Later, he brought this one back to the Brooklyn Navy Yards. In the form of compounds, iron is found everywhere. It is the most common coloring agent in rocks and soils, and exists in many food products and in the blood.

3. **Reduction of Iron.**—It will be remembered that zinc is reduced from its chief ore by means of coke, after the preliminary roasting has converted the sulphide into an oxide. Since most of the iron ores are already oxides, this preliminary treatment is not necessary. Coke is used to furnish the heat and the carbon for the reduction.

4. **The Blast Furnace.**—The ordinary blast furnace varies from 20 to 25 feet in diameter and from 75 to 90 feet in height. It is made of fire brick and strength-

ened on the outside by heavy boiler plate iron. The top of the furnace is so constructed that it is practically air-tight, and any gases formed within must pass off through a pipe near the top shown in Fig. 70. However, as the process is a continuous one, additions of

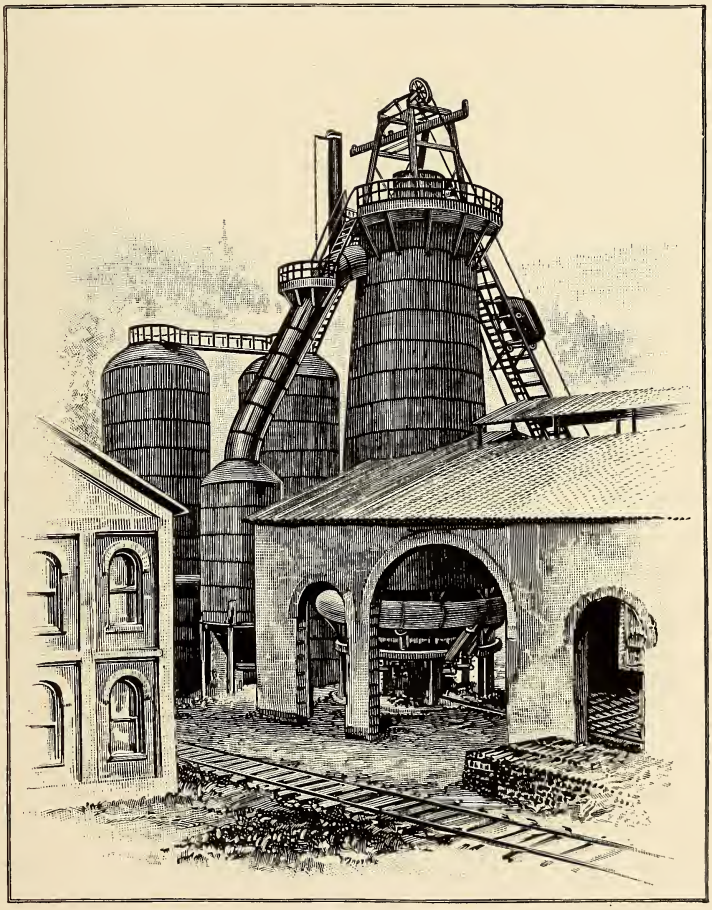


Fig. 70.—A blast furnace for preparing cast iron.

material are made repeatedly through a hopper which opens mechanically when a load is dumped upon it and then closes again when the material has fallen into the furnace. Near the bottom is an opening for drawing off the molten iron, which is kept closed by means of clay until needed. At some distance above is an opening for the exit of the slag. As the quantity is usually large, this is open most of the time with a steady outflow of the molten material. Above this, entering from the sides, are the blast pipes, often called *tuyeres*, through which the air is forced into the furnace. This is needed to give the intense heat required. The furnace is tapped usually every twelve hours and the molten iron run off into trenches and side trenches in the ground. These short trenches are called "pigs" and the iron formed in them "pig iron." Sometimes the molten iron is run into steel molds bolted upon an endless chain, which moves slowly forward as each is filled from a large cauldron. (See Fig. 71 for illustration of method of molding pig iron.)

5. **The Charge.**—The materials used in the "charge" put into the furnace are usually iron ore, coke and limestone. Most ores when brought from the mine contain more or less silica. In the furnace the limestone with the silica forms a species of glass, called *slag*. It floats above the molten metal and protects it from the oxidizing action of the blasts of air. When the ore contains limestone as a *gangue*, instead of silica, some silicious material is added to serve as the flux.

6. **The Chemical Action.**—Owing to the large amount of air introduced through the tuyeres, at the bottom of the furnace carbon dioxide is produced. (See p. 169.) As this flows upward it meets red-hot carbon and is changed to carbon monoxide, thus,

$$CO_2 + C \rightarrow 2CO.$$

This being an unsaturated gas removes the oxygen from the iron ore and the free iron thus produced flows to the bottom of the furnace. The gas, which escapes at the top, contains much carbon monoxide as well as other combustible gases. This is used to heat the air forced

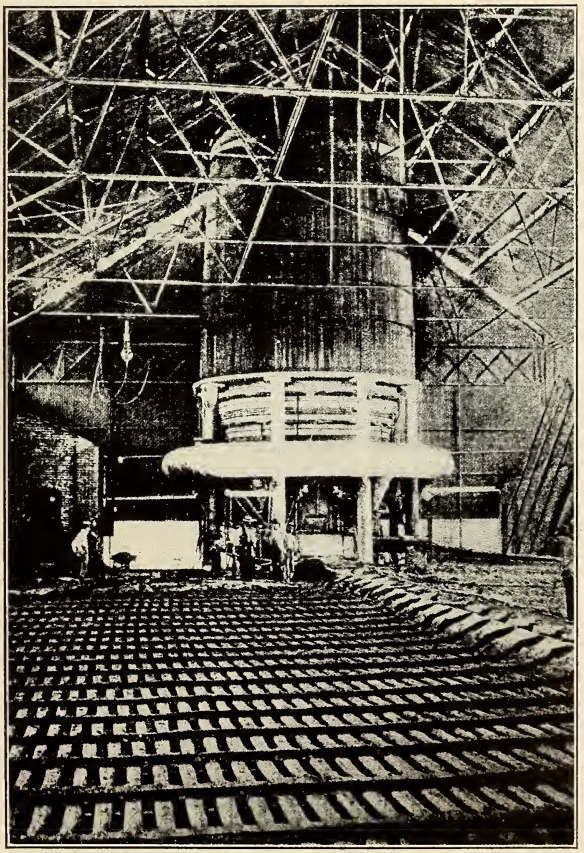


Fig. 71.—A blast furnace, showing the molds for the "pigs" in the sand.

in and to run the fans for the air pressure. The iron thus obtained is known as *cast iron*. It contains a high percentage of carbon, sometimes as much as 3 or 4 per cent as well as silica and other impurities. It is coarse grained, brittle, hard, and has a melting point relatively low, about 1250° C.

7. **Wrought Iron.**—Wrought iron is made by heating the cast iron in a reverberatory furnace with ferric oxide. The purpose of the oxide is to furnish oxygen for union with the carbon in the iron, by which carbon monoxide is formed. These are sometimes called *puddling* furnaces, because the molten pig iron is "puddled" or stirred so as to facilitate the action. When the mass has become stiff and very difficult to stir, it is known that the carbon is burned out. Pure iron melts with much more difficulty than impure, and the temperature of these furnaces is only sufficient to keep the impure form in a molten condition. It is the same principle, seen often before, in which a solution will remain liquid while the solvent will solidify. At this stage the iron, called "bloom," is removed from the furnace, and beaten with trip hammers, which forces out the silica and any slag remaining. Such is now *wrought iron*. It is malleable and may be welded; it is fine grained, somewhat more dense than cast iron, melts at about 1,500° C. and contains only about 0.1 to 0.2 per cent of carbon. It should not contain much phosphorus or sulphur. Wrought iron is made into sheets, and is used in chains, wire, and in many other ways where a cheap, malleable metal is desired.

8. **Steel.**—The oldest method of making steel was by the *cementation* process. Bars of wrought iron were imbedded in powdered charcoal and heated strongly for a number of days. The iron slowly absorbed small portions

of the carbon and was changed thereby into steel. However, it was far from satisfactory, for the reason that the carbon was not taken up uniformly. Some portions would contain so much as to be more or less brittle, while others would not contain enough. *Cast steel* was first made by melting cementation steel and molding it into a bar so as to give uniform composition. This greatly improved the produce previously obtained. The process is entirely too slow for modern demands; for years, until recently, most of the steel used has been made by the *Bessemer* process

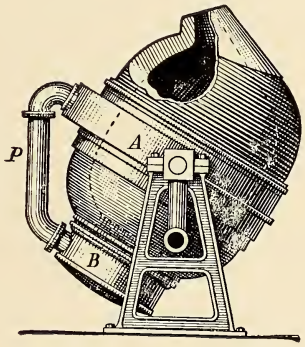



Fig. 72.—The Bessemer converter.

(Fig. 72). This process uses a movable furnace, called a *converter,* made of boiler-plate iron and lined with a silicious earth called *ganister,* which is infusible. The compressed air passes up through a supporting post, through the horizontal trunnion, and down the pipe into the tuyere box or air chamber, then into the body of the converter. For use it is filled half or two-thirds with molten cast iron and the air is turned on. No heat is applied; the interaction of the oxygen of the air with the carbon and other impurities in the iron is sufficient not only to keep the metal molten, but even raise the temperature.

At first luminous flames and great showers of sparks shoot from the mouth of the converter, but as the carbon is burned out the action becomes more quiet until finally it practically ceases altogether. If the product obtained at this stage were hammered, it would form wrought iron. For steel a definite amount of *spiegel iron* is added. This is an iron-manganese alloy which may have as high as 20 per cent of manganese, but usually only a small proportion. It contains also a fixed amount of carbon so that any required proportion of carbon may be thus put back into the iron to form the steel. The blast of air is continued just long enough to mix the spiegel thoroughly with the other when the whole is poured out and cast into ingots. It will be seen that the process consists in burning out *all* the carbon and then restoring whatever may be desired for a particular variety of steel. This method works successfully unless phosphorus be present in the cast iron. The Bessemer converter will not remove phosphorus, and its presence makes steel brittle. To remove it, a converter lined with lime is used. Phosphorus, being an acidic element, unites with the lime, a basic oxide, forming the superphosphate of calcium, mentioned on p. 281 as a valuable fertilizer. This modified plan is called the *basic lining* or the *Thomas-Gilchrist process.*

9. **Open Hearth Steel.**—In the last few years much steel has been made by what is known as the *open hearth* or *Siemens-Martin* process. The cast iron, whose carbon content is known by chemical analysis, is mixed with a definite amount of hematite, ferric oxide, or some other iron ore, and heated in an open furnace with a gaseous fuel, for about ten hours. The materials are so proportioned as to leave a definite amount of carbon in the steel. The gas used for fuel is heated before being burned and the

charge is tested from time to time to know when the process is complete.

10. **Characteristics of Steel.**—Steel is between wrought and cast iron in content of carbon. The amount varies from 0.5 to 1.5 per cent. Its most remarkable property is its ability to be *tempered*, that is, to be so treated as to hold a *cutting edge*. It also has wonderful tensile strength. Wires of lead, copper and steel, of equal diameter, show that steel will withstand twice what copper will and forty times what lead will. This is one of the chief reasons for the great use of steel in the arts.

11. **Tempering Steel.**—If a piece of steel is heated to redness and then cooled slowly it is soft and malleable like wrought iron; but if so heated and cooled suddenly it is hard and brittle. Now if it be heated again to a much lower temperature, ranging from 225° to 325° C., it assumes degrees of hardness and brittleness between these two conditions and is suitable for cutting instruments. At the lower temperature, such keen-edged instruments as razors and instruments employed in surgery are made; at the higher, saws and similar tools. The explanation of this, put as simply as possible, is as follows. At the temperature first used a considerable amount of iron carbide is formed which makes the steel brittle. If the bar is cooled suddenly the carbide remains in the steel; if cooled slowly the carbide decomposes and leaves less of it in the steel. At the second heating, if only a low temperature is used, not so much time is given in cooling for the iron carbide to be decomposed; hence, a considerable amount remains and the steel is harder and takes a keener edge, but is more brittle. When heated to a higher temperature more time is given for the carbide to be decomposed; hence, the steel is left softer, less brittle and better

suited for rough tools, but not capable of so keen an edge.

12. **Kinds of Steel.**—By mixing in the converter one or more of some of the rarer metals, alloys of great value may be obtained. As they consist mainly of steel they are spoken of as such. *Chrome steel* contains a small percentage of chromium or sometimes both chromium and vanadium. It is a steel of special strength and is used in parts of machinery where great strain may come, as in the axles and frames of motor cars. *Nickel steel* may contain as much as 4 per cent of nickel and is especially desirable as armor for war vessels. It has great strength, is very tenacious, hard to pierce with projectiles, and resistant to sea water. A *manganese steel* gives a variety used for making burglar proof safes of very great hardness.

13. **General Characteristics of Iron.**—The most important physical properties have been given in describing the different varieties of iron. It is well up in the electromotive series of metals and readily displaces hydrogen from dilute acids. Very concentrated nitric acid products a singular condition known as the *passive state* in which it will not react with dilute acids with the evolution of hydrogen. Chromium is affected in a similar manner. Hammering will restore its former properties. In oxygen, iron when heated burns readily with a beautiful shower of sparks, and forms mainly the magnetic oxide, $Fe_3O_4$. Superheated steam, directed upon iron, gives it a blue color due to the formation of a closely-adhering, protecting film of this same oxide. In the air, in the presence of moisture, ferric oxide, $Fe_2O_3$, is formed; this being nonadhering, the metal becomes entirely corroded.

14. **Compounds of Iron.**—Iron forms two classes of compounds, ferrous and ferric. The former are mostly green in color, the latter brown. Ferrous compounds are unsaturated and, as a rule, tend to become oxidized to the ferric.

Ferrous sulphate, $FeSO_4.7H_2O$, is commonly known by the name of green vitriol, or copperas. It is an efflorescent hydrate, but as it loses its water, it also becomes oxidized from the air and forms a basic ferric sulphate. Therefore, unlike effloresced blue vitriol, the addition of water does not re-form the ferrous sulphate. It is used in various ways. Common black ink is a mixture of ferrous sulphate and tannic acid, which on exposure changes into a black ferric salt. To give it more body some mucilage is usually added and often some dye as well. Ferrous chloride, $FeCl_2$, may be made by dissolving iron in dilute hydrochloric acid. It is a very unstable salt and rapidly oxidizes to a ferric. Ferrous hydroxide, $Fe(HO)_2$ may be prepared by adding, to any soluble ferrous salt, a solution of some alkali. If pure it is white in color, but as usually obtained is greenish, changing rapidly to brown as it is oxidized by the air. The double salt, ferrous ammonium sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, is the most stable of the ferrous salts. It is pale green in color, crystalline in structure and soluble in water. For experimental work in the laboratory it is far the best for use.

15. **Ferric Compounds.**—Ferric chloride, $FeCl_3.6H_2O$, is a very deliquescent, brown solid. It is employed in most pharmaceutic preparations of iron. Mention has been made of its use in preparing the best antidote for arsenic. Ferric sulphate, $Fe_2(SO_4)_3$, may be made by the oxidation of ferrous sulphate with nitric acid or bromine or with some other oxidizing agent. Ferric hy-

droxide, $Fe(HO)_3$, may be prepared by treating ferric chloride with ammonium hydroxide or any other soluble hydroxide. It is a gelatinous, brownish colored precipitate. Heated, it loses water and becomes ferric oxide, $Fe_2O_3$.

16. **Oxidation and Reduction of Iron Compounds.**—As stated above, ferrous salts may be readily changed to ferric by oxidation. If a solution of ferrous sulphate acidulated with sulphuric acid has nitric acid added and is then heated, it is changed into ferric sulphate, thus,

$$2FeSO_4 + H_2SO_4 + 2HNO_3 \rightarrow Fe_2(SO_4)_3 + 2H_2O + 2NO_2.$$

Potassium permanganate is used to oxidize ferrous salts to ferric in the same way. As it is of a deep violet, a coloration of the iron solution is seen as soon as the oxidation is completed. A permanganate solution, therefore, of known strength, may be used to determine the amount of iron present, by noting the number of cubic centimeters needed to oxidize a certain amount of the ferrous solution. The equation is

$$2KMnO_4 + 8H_2SO + 10FeSO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Conversely, ferric salts may be reduced to ferrous. This is easily done by nascent hydrogen, thus,

$$2FeCl_3 + 2H \rightarrow 2FeCl_2 + 2HCl.$$

The hydrogen may be obtained by putting pieces of zinc into the ferric solution and adding a dilute acid as hydrochloric. In a similar way hydrogen sulphide reduces iron salts in the presence of an acid, thus,

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S.$$

The sulphur is precipitated.

17. **Other Iron Compounds.**—There are a few compounds in which iron forms a part of the negative ion. Such are potassium ferrocyanide, $K_4Fe(CN)_6$, and ferri-

cyanide, $K_3Fe(CN)_6$. These were formerly regarded as double salts as their present names indicate. Potassium *ferrous* cyanide was regarded as $Fe(CN)_2.4KCN$ and the other as $Fe(CN)_3.3KCN$. If really double salts, as last written, the former would in solution contain ferrous ions, and the latter ferric ions. Chemical tests show this is not true. Mixed with ferric or ferrous salts, they give compounds, one of which is known as Prussian blue, $Fe_4[Fe(CN)_6]_3$, which was formerly used frequently instead of indigo as a cheap bluing in laundry work. Both of the cyanide compounds have use in the laboratory in making delicate tests for the presence of iron.

18. **Some Pigments.**—*Rouge* is the commercial name for a form of ferric oxide used in polishing. It is made from ferrous sulphate which is obtained in cleaning iron for the purpose of galvanizing. *Venetian Red* and other cheap red pigments, used for painting roofs and outbuildings, are largely ferric oxide mixed with more or less clay. *Yellow ochre* is a hydrated form of the same compound and corresponds to limonite, already mentioned. It is used sometimes for priming woodwork and as a cheap paint. *Raw* and *burnt sienna* and *raw* and *burnt umber* are other well-known pigments of similar composition, two of them obtained, as the names indicate by strongly heating the oxide.

19. **Nickel, its Characteristics.**—Nickel is a hard white metal which tarnishes very slowly in the air. It is susceptible of a high polish. It is little attacked either by dilute hydrochloric or sulphuric acid. It is extensively used in plating iron. The method is the same as described in the case of the other metals, except a different solution of nickel is used. The double sulphate of nickel and ammonium, $(NH_4)_2SO_4.NiSO_4.6H_2O$, gives a plating which adheres best. It is a greenish colored salt, soluble in water. Nickel is also used in coin-

age, alloyed with copper in the familiar five-cent piece; in the powdered form it is used somewhat in wireless telegraphy and in the familiar alloy, German silver. Its use in making nickel steel has been mentioned as well as its catalytic action in the hydrogenation of oils.

20. **Compounds of Nickel.**—Nickel forms two series of compounds, nickelous and nickelic. The former are the more common. They are mostly green in color; however, fused in the borax bead, they give a brown coloration, which is distinctive. The most important salt is the double sulphate already mentioned as of use in plating.

21. **Characteristics of Cobalt.**—Cobalt is a hard, white metal resembling nickel. It has no uses. It forms two classes of compounds, cobaltous and cobaltic. The former are the more common and the more important. They are deep pink or reddish in color. Fused in a borax bead, even in minute quantity, they give a beautiful blue color, which serves to identify the metal.

22. **Uses of Cobalt Compounds.**—Some very valuable pigments are made from cobalt compounds. *Smalt*, a kind of glass, made by fusing some cobalt compound as the oxide, with sand and potassium nitrate, is of a deep blue color. It is powdered and mixed in the paste used on the outside of iron vessels in the manufacture of "granite ware." When these are heated strongly in ovens the coating melts and gives the familiar blue ware in common use. It is also ground in oil and used as a paint for chinaware. Several cobalt salts become blue in color when they lose their water of combination. Based upon this fact is the "cobalt barometer" occasionally seen. It consists of a strip of unsized paper or cloth moistened with cobaltous solution. If the air is very dry the paper turns blue; if damp, red. Sympathetic inks, containing some cobalt compound, depend upon the same property.

When used upon paper the pink color is scarcely visible; if warmed, the water of combination is removed and the compound turns blue. It then may be plainly read. In damp air it will again become invisible.

### Exercises for Review

1. Name the metals usually associated with iron. Why do they not form a periodic group?

2. Mention the chief ores of iron and give composition.

3. How could you recognize a piece of hematite? Of limonite?

4. Describe the construction of the blast furnace.

5. Of what does the charge put into a blast furnace consist? What is the purpose of each?

6. Describe the chemical action which takes place in the blast furnace.

7. How is wrought iron made? What are some of its uses?

8. Describe the cementation process of making steel. Why was cast steel used?

9. Describe the Bessemer converter and state the principle underlying its use.

10. What is the Thomas-Gilchrist process of making steel?

11. Describe the open hearth process.

12. How is steel tempered? Explain the principle underlying.

13. Name some different kinds of steel and state for what adapted.

14. Give the chemical properties of iron. What is meant by the passive state?

15. What is green vitriol? How made? Uses? Name some other ferrous compound.

16. Name one ferric salt and tell how to prepare ferric hydroxide from it. What use has the hydroxide?

17. How can ferrous sulphate be changed to ferric? Ferric chloride to ferrous? What is oxidation in the broad sense?

18. Name some common iron pigments and give uses for them. Of what do they consist?

19. Give the chief characteristics of nickel and uses.

20. How is nickel plating done?

21. Name one important compound of cobalt and give important use for it.

22. What is a sympathetic ink? Explain how one made from cobalt compounds works.

## CHAPTER XXXVII

## THE PLATINUM AND PALLADIUM GROUPS

**Outline—**

Members of the Group
Occurrence
Platinum
(*a*) Characteristics
(*b*) Uses
Osmium
Iridium
Palladium

1. **Members of the Group.**—Osmium, iridium and platinum are associated as are iron, nickel and cobalt, but do not constitute a periodic group, for their weights run consecutively and not as octaves. Osmium has an atomic weight of 191, iridium, 193, and platinum, 194.8.

2. **Occurrence.**—These metals are found as grains or small nuggets in alluvial deposits, much as is gold, but in very limited quantities. California produces about all there is obtained in the United States. Nearly the entire world's supply comes from the Ural Mountains in eastern Russia. The three metals are nearly always found mixed together, with platinum the more abundant. They are separated by difficult chemical processes which would not be of interest to the student.

3. **Characteristics of Platinum.**—Platinum is the most important metal of the group. It is steel-white in color, very hard, not attacked by acids, but is soluble in aqua regia, or nascent chlorine. It is exceedingly malleable and ductile, and when heated may be welded like wrought iron. At red heat it easily forms alloys with

metals of low melting point, such as lead and antimony and will also combine with carbon, phosphorus and silica. The alloys mentioned have low melting points; hence, the greatest care must be exercised not to heat any such metals in platinum ware. If it is done, the alloy is readily formed, and then melts out leaving a hole in the platinum vessel. Silica and phosphorus render platinum brittle, so may likewise cause serious injury. If pure, platinum has a high melting point of about 1,700° C. When finely divided it has great power of occluding or absorbing hydrogen. It frequently possesses the power of catalysis. This has already been seen in several instances. It may likewise be shown by holding a spiral of platinum wire in the neck of a flask of strong ammonium hydroxide, slightly warmed. If the wire is heated before being thrust into the neck of the flask at some point where the ammonia and air are mixed, the wire will become red hot and so continue as long as the current of ammonia is escaping. The wire may even be withdrawn from the flask and reinserted when it will again heat up as before.

4. **Uses of Platinum.**—On account of its high melting point and resistance to attack by acids, platinum is employed extensively in the laboratory in the form of crucibles, wire and foil. In late years, unfortunately for science, it has been used very largely in jewelry. Catalytically, it is used in making sulphuric acid by the contact process (p. 261) as well as in other manufacturing processes. In dentistry platinum wire is used as "posts" in fastening artificial teeth to the plate. It is also used in electric lamps as the connection between the inside filament and the outside copper wire. This is for the reason that platinum has practically the same rate of expansion when heated as glass: any metal used

thus which expands more than glass when heated by the current would crack the lamp.

5. **The Other Metals of the Group.**—Osmium is remarkable for its high melting point, being over 2,000° C. Iridium is harder than platinum and is sometimes alloyed with the latter for the purpose of securing a metal with extreme resistance to acids. It is also sometimes used on the tips of fountain pens. Palladium is of special interest because of its remarkable power of absorbing hydrogen and other gases. When heated it will occlude about seven hundred times its own volume of hydrogen. It does not belong with the platinum metals, but is the most important metal of another special group, much lighter in weight.

### Exercises for Review

1. Name the metals of the platinum group and give atomic weights.
2. Why can these three not be regarded as forming a periodic group?
3. What can you say of the occurrence of the metals of this group?
4. Give the important characteristics of platinum.
5. What precaution must be taken regarding heating low-melting metals in a platinum vessel?
6. What other substances also injure platinum seriously?
7. In what way have you seen platinum used in chemical experiments? Why is it used frequently in the chemical laboratory?
8. Name some other valuable uses for platinum in the arts.
9. Why should platinum not be used for jewelry?
10. Give some one point of interest about osmium, iridium and palladium. Give some use for iridium.
11. Where does palladium belong in the table? What other metals are associated with it?

# TABLES FOR REFERENCE AND GLOSSARY

### Solubilities of Common Compounds

It may be desirable to know at times whether a compound is soluble in water. A few general rules may be helpful and are given below.

(a) All salts of the sodium group, including those of ammonium are soluble, with the exception of two or three very uncommon ones.

(b) All bromides are soluble except those of lead, mercury, and silver.

(c) All carbonates of the sodium group, including ammonium, are soluble; all others are insoluble.

(d) All chlorates are soluble.

(e) All chlorides are soluble except lead chloride, mercurous chloride, and silver chloride.

(f) The hydroxides of the sodium group, ammonium, and the calcium group are soluble, calcium only moderately so, while all others are insoluble.

(g) All nitrates are soluble.

(h) The oxides of the sodium and calcium group are chemically soluble in water, that is, they react to form a new compound, the hydroxide. All other oxides are insoluble in water.

(i) Phosphates are insoluble except those of the alkali metals and ammonium.

(j) Silicates are insoluble except those of the alkalies and ammonium. Even then if mixed with silicates of heavier metals they are insoluble.

(k) The sulphates of barium, calcium, lead and strontium are insoluble; others are soluble.

## Some Interesting Temperatures

| | |
|---|---|
| Absolute zero | −273° C |
| Hydrogen melts | −260 |
| Hydrogen boils | −252.6 |
| Nitrogen melts | −214 |
| Nitrogen boils | −194 |
| Oxygen boils | −182.5 |
| Alcohol freezes | −130 |
| Mercury freezes | − 39.5 |
| Water freezes | 0 |
| Room temperature | 21 |
| Ether boils | 34.6 |
| Human body | 37 |
| Wood's Metal melts | 60 |
| Alcohol boils | 78.5 |
| Water boils | 100 |
| Sulphur melts (rhomb) | 114.5 |
| Tin melts | 232 |
| Lead melts | 327 |
| Mercury boils | 357 |
| Zinc melts | 419 |
| Dull red heat | 650 |
| Aluminum melts | 660 |
| Bright red heat | 1,000 |
| Gold melts | 1,064 |
| White heat | 1,350 |
| Iron melts | 1,520 |
| Platinum melts | 1,750 |
| Corundum melts | 2,000 (about) |
| Oxyhydrogen flame | 2,500 |
| Oxyacetylene flame | 2,700 |
| Tungsten melts | 3,000 |
| Thermit gives | 3,500 (about) |
| Electric arc | 4,000 (about) |

## Tables of Weights and Measures

### Weights

| | |
|---|---|
| 10 milligrams (mg.) | = 1 centigram (cg.) |
| 10 centigrams | = 1 decigram (dg.) |
| 10 decigrams | = 1 gram (g.) |
| 1,000 grams | = 1 kilogram (kg.) |

### English Equivalents

| | |
|---|---|
| 1 kilogram | = 2.2046 pounds |
| 28.35 grams | = 1 ounce |
| 1 gram | = 15.43 grains |
| 500 grams | = 1.1023 pounds |

The unit of weight in the Metric System is the gram.

### Volumes

| | |
|---|---|
| 1,000 cubic centimeters (c.c.) | = 1 liter |
| 1 cubic decimeter (c.d.) | = 1 liter |
| 1 liter (l.) | = 1.056 liquid quarts |

The unit in the Metric System is the liter.

### Length

| | |
|---|---|
| 10 millimeters (mm.) | = 1 centimeter (cm.) |
| 10 centimeters | = 1 decimeter (dm.) |
| 10 decimeters | = 1 meter (m.) |

### English Equivalents

| | |
|---|---|
| 1 centimeter | = 0.3937 inches |
| 2.54 centimeters | = 1.0 inch |
| 1 meter | = 39.37 inches |

### Thermometer Equivalents

For scientific work the centigrade thermometer is always used and readings given in scientific books are always centigrade unless otherwise specified. Freezing water is 0° C. and boiling point is 100° C.

0 Centigrade is 32 Fahrenheit and 273 Absolute
100 " " 212 " " 373 "
One degree Centigrade = 9/5 of a degree Fahrenheit
One degree Fahrenheit = 5/9 of a degree Centigrade
One degree Centigrade = One degree Absolute

To convert centigrade degrees into Fahrenheit, multiply by 9/5 and add 32, algebraically. This means that if the centigrade reading is below zero, it would have the minus sign and one would be

substracted from the other. To convert Fahrenheit readings into centigrade multiply by 5/9 after substracting 32 from the Fahrenheit reading.

LIST OF ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS. (O=16.)
(The more important elements are printed in heavy type.)

| NAME OF ELEMENT | SYMBOL | ATOMIC WEIGHT | NAME OF ELEMENT | SYMBOL | ATOMIC WEIGHT |
|---|---|---|---|---|---|
| **Aluminum** | Al | 27.1 | Molybdenum | Mo | 96.0 |
| Antimony | Sb | 120.2 | Neodymium | Nd | 144.3 |
| Argon | A | 39.88 | Neon | Ne | 20.2 |
| **Arsenic** | As | 74.96 | **Nickel** | Ni | 58.68 |
| **Barium** | Ba | 137.37 | Niton | Nt | 222.4 |
| **Bismuth** | Bi | 208.0 | **Nitrogen** | N | 14.01 |
| **Boron** | B | 11.0 | Osmium | Os | 190.9 |
| **Bromine** | Br | 79.92 | **Oxygen** | O | 16.00 |
| Cadmium | Cd | 112.4 | Palladium | Pd | 106.7 |
| Cæsium | **Cs** | 132.81 | **Phosphorus** | P | 31.04 |
| **Calcium** | Ca | 40.07 | **Platinum** | Pt | 195.2 |
| **Carbon** | C | 12.00 | **Potassium** | K | 39.1 |
| Cerium | Ce | 140.25 | Praseodymium | Pr | 140.6 |
| **Chlorine** | Cl | 35.46 | **Radium** | Ra | 226.4 |
| **Chromium** | Cr | 52.0 | Rhodium | Rh | 102.9 |
| **Cobalt** | Co | 58.97 | Rubidium | Rb | 85.45 |
| Columbium | Cb | 93.5 | Ruthenium | Ru | 101.7 |
| **Copper** | Cu | 63.57 | Samarium | Sa | 150.4 |
| Dysprosium | Dy | 162.5 | Scandium | Ss | 44.1 |
| Erbium | Er | 167.7 | Selenium | Se | 79.2 |
| Europium | Eu | 152.0 | **Silicon** | Si | 28.3 |
| **Fluorine** | F | 19.0 | **Silver** | Ag | 107.88 |
| Gadolinium | Gd | 157.3 | **Sodium** | Na | 23.00 |
| Gallium | Ga | 69.9 | **Strontium** | Sr | 87.63 |
| Germanium | Ge | 72.5 | **Sulphur** | S | 32.07 |
| Glucinum | Gl | 9.1 | Tantalum | Ta | 181.5 |
| **Gold** | Au | 197.2 | Tellurium | Te | 127.5 |
| Helium | He | 3.99 | Terbium | Tb | 159.2 |
| Holmium | Ho | 163.5 | Thallium | Tl | 204.0 |
| **Hydrogen** | H | 1.008 | Thorium | Th | 232.4 |
| Indium | In | 114.8 | Thulium | Tm | 168.5 |
| **Iodine** | I | 126.92 | **Tin** | Sn | 119.0 |
| Iridium | Ir | 193.1 | Titanium | Ti | 48.1 |
| **Iron** | Fe | 55.84 | **Tungsten** | W | 184.0 |
| Krypton | Kr | 82.92 | Uranium | U | 238.5 |
| Lanthanum | La | 139.0 | Vanadium | V | 51.0 |
| **Lead** | Pb | 207.1 | Xenon | Xe | 130.2 |
| **Lithium** | Li | 6.94 | Ytterbium | Yb | 172.0 |
| Lutecium | Lu | 174.0 | Yttrium | Yt | 89.0 |
| **Magnesium** | Mg | 24.32 | **Zinc** | Zn | 65.37 |
| **Manganese** | Mn | 54.93 | Zirconium | Zr | 90.6 |
| **Mercury** | Hg | 200.6 | | | |

## Names and Formulas of the More Common Chemicals

| | |
|---|---|
| Acetic acid | $HC_2H_3O_2$ |
| Alcohol | $C_2H_5OH$ |
| Alum, ammonium | $(NH_4)_2Al_2(SO_4)_4$ |
| Alum, potassium | $K_2Al_2(SO_4)_4$ |
| Aluminum oxide | $Al_2O_3$ |
| Aluminum sulphate | $Al_2(SO_4)_3$ |
| Ammonium bicarbonate | $NH_4HCO_3$ |
| " carbonate | $(NH_4)_2CO_3$ |
| " chloride | $NH_4Cl$ |
| " hydroxide | $NH_4OH$ |
| " nitrate | $NH_4NO_3$ |
| " sulphate | $(NH_4)_2SO_4$ |
| Antimony oxychloride | $SbOCl$ |
| " trichloride | $SbCl_3$ |
| " trisulphide | $Sb_2S_3$ |
| Arsenic trioxide | $As_2O_3$ |
| Barium carbonate | $BaCO_3$ |
| " chloride | $BaCl_2$ |
| " dioxide | $BaO_2$ |
| " hydroxide | $Ba(OH)_2$ |
| " nitrate | $Ba(NO_3)_2$ |
| " oxide | $BaO$ |
| " sulphate | $BaSO_4$ |
| Bismuth chloride | $BiCl_3$ |
| " nitrate | $Bi(NO_3)_3$ |
| " subnitrate | $BiONO_3$ |
| " trioxide | $Bi_2O_3$ |
| Bleaching powder | $CaCl(OCl)$ |
| Borax | $Na_2B_4O_7$ |
| Calcium carbide | $CaC_2$ |
| " carbonate | $CaCO_3$ |
| " chloride | $CaCl_2$ |
| " fluoride | $CaF_2$ |
| " hydroxide | $Ca(OH)_2$ |
| " oxide (lime) | $CaO$ |
| " phosphate | $Ca_3(PO_4)_2$ |
| " sulphate | $CaSO_4$ |
| Carbolic acid | $C_6H_5OH$ |
| Carbon disulphide | $CS_2$ |

| | |
|---|---|
| Chloroform | $CHCl_3$ |
| Chrome yellow | $PbCrO_4$ |
| Cinnabar | $HgS$ |
| Copper acetate | $Cu(C_2H_3O_2)_2$ |
| " chloride | $CuCl_2$ |
| " nitrate | $Cu(NO_3)_2$ |
| " oxide | $CuO$ |
| " sulphate | $CuSO_4$ |
| " sulphide | $CuS$ |
| Ether, sulphuric | $(C_2H_5)_2O$ |
| Ferric chloride | $Fe_2Cl_6$ |
| " hydroxide | $Fe_2(OH)_6$ |
| " nitrate | $Fe_2(NO_3)_6$ |
| " oxide | $Fe_2O_3$ |
| Ferrous sulphate | $FeSO_4$ |
| Ferrous sulphide | $FeS$ |
| Fluor spar | $CaF_2$ |
| Gold trichloride | $AuCl_3$ |
| Hydrochloric acid | $HCl$ |
| Hydrofluoric acid | $HF$ |
| Hydrogen peroxide | $H_2O_2$ |
| Hydrogen sulphide | $H_2S$ |
| Hypochlorous acid | $HClO$ |
| Iodic acid | $HIO_3$ |
| Iodoform | $CHI_3$ |
| Lead acetate | $Pb(C_2H_3O_2)_2$ |
| " carbonate | $PbCO_3$ |
| " chloride | $PbCl_2$ |
| " chromate | $PbCrO_4$ |
| " nitrate | $Pb(NO_3)_2$ |
| " oxide (litharge) | $PbO$ |
| " sulphate | $PbSO_4$ |
| Lime | $CaO$ |
| Litharge | $PbO$ |
| Lithium chloride | $LiCl$ |
| Magnesia | $MgO$ |
| Magnesium carbonate | $MgCO_3$ |
| " chloride | $MgCl_2$ |
| " oxide | $MgO$ |
| " sulphate | $MgSO_4$ |
| Manganese dioxide | $MnO_2$ |

| | |
|---|---|
| Mercuric chloride | $HgCl_2$ |
| " iodide | $HgI_2$ |
| " nitrate | $Hg(NO_3)_2$ |
| " oxide | $HgO$ |
| " sulphide | $HgS$ |
| Mercurous chloride | $Hg_2Cl_2$ |
| " iodide | $Hg_2I_2$ |
| " nitrate | $Hg_2(NO_3)_2$ |
| Minium | $Pb_3O_4$ |
| Phosphine | $PH_3$ |
| Phosphorus pentoxide | $P_2O_5$ |
| Plaster of Paris | $CaSO_4.H_2O$ |
| Platinum tetrachloride | $PtCl_4$ |
| Potassium acetate | $KC_2H_3O_2$ |
| " bicarbonate | $KHCO_3$ |
| " bromide | $KBr$ |
| " carbonate | $K_2CO_3$ |
| " chlorate | $KClO_3$ |
| " chloride | $KCl$ |
| " chromate | $K_2CrO_4$ |
| " cyanide | $KCN$ |
| " dichromate | $K_2Cr_2O_7$ |
| " ferricyanide | $K_3Fe(CN)_6$ |
| " ferrocyanide | $K_4Fe(CN)_6$ |
| " hydroxide | $KOH$ |
| " iodide | $KI$ |
| " nitrate | $KNO_3$ |
| " nitrite | $KNO_2$ |
| " permanganate | $KMnO_4$ |
| " sulphate | $K_2SO_4$ |
| " sulphocyanate | $KSCN$ |
| Silica | $SiO_2$ |
| Silver bromide | $AgBr$ |
| " chloride | $AgCl$ |
| " iodide | $AgI$ |
| " nitrate | $AgNO_3$ |
| Sodium acetate | $NaC_2H_3O_2$ |
| " arseniate | $Na_3AsO_4$ |
| " arsenite | $NaAsO_2$ |
| " bicarbonate | $NaHCO_3$ |
| " carbonate | $Na_2CO_3$ |

| | |
|---|---|
| Sodium chloride | $NaCl$ |
| " hydroxide | $NaOH$ |
| " iodide | $NaI$ |
| " nitrate | $NaNO_3$ |
| " nitrite | $NaNO_2$ |
| " phosphate | $Na_2HPO_4$ |
| " sulphate | $Na_2SO_4$ |
| " sulphide | $Na_2S$ |
| " sulphite | $Na_2SO_3$ |
| " thiosulphate | $Na_2S_2O_3$ |
| Stannic chloride | $SnCl_4$ |
| " oxide | $SnO_2$ |
| Stannous chloride | $SnCl_2$ |
| Strontium nitrate | $Sr(NO_3)_2$ |
| Sulphur dioxide | $SO_2$ |
| Sulphuric acid | $H_2SO_4$ |
| Sulphurous acid | $H_2SO_3$ |
| Sulphur trioxide | $SO_3$ |
| Zinc chloride | $ZnCl_2$ |
| " oxide | $ZnO$ |
| " sulphate | $ZnSO_4$ |

# GLOSSARY

## Chemical Terms

**Actinic.** Actinic light rays are those which have the power of producing chemical change in substances, as upon a photographic plate.

**Alkali.** A soluble hydroxide, with caustic properties, sharp biting taste, and power of corroding the skin.

**Allotropic.** Literally, another form of an element; more often applied to the unusual form. Ozone as related to oxygen.

**Alloy.** A mixture of two or more metals, melted together so as to be homogeneous. Example, brass.

**Amalgam.** An alloy, one component of which is mercury.

**Amorphous.** Without special form; unerystallized.

**Anesthetic.** A substance used to produce unconsciousness.

**Anhydride.** An acidic oxide. An oxide forming an acid on the addition of water.

**Anhydrous.** Without water.

**Antiseptic.** An antiseptic is a substance used to prevent decay or destroy pathogenic bacteria.

**Basic.** Having the properties of a base or alkali.

**Binary.** A compound consisting of two elements.

**Calcine.** To heat strongly.

**Commercial.** A term applied to chemicals not pure but sufficiently so for all ordinary uses.

**C. P.** Chemically pure. Applied to a better grade of chemicals than those marked "commercial."

**Decant.** To pour off a liquid from a precipitate.

**Deliquesce.** To gather moisture from the air and become liquid.

**Desiccator.** A vessel used for drying substances.

**Destructive Distillation.** Heating a substance in a closed retort so as to decompose it and produce new substances; as in distilling coal.

**Downward Displacement.** Collecting a gas heavier than air by letting it flow *downward* into a bottle full of air, thus *displacing* the air.

**Distillate.** The liquid obtained by distillation.

**Dyad.** An element with valence of two.

**Effloresce.** To give up water of combination at room temperature and become a powder.

**Electrode.** The terminal of a battery.

**Empirical.** Applied to a formula which shows composition only. Not structural.

**Escharotic.** A caustic. A substance which corrodes.

**Filtrate.** The liquid which passes through a filter.

**Flocculent.** Flaky; often applied to certain precipitates.

**Flux.** A substance used to lower the melting point of some substance: often it is a solvent for the substance.

**Fractional Distillation.** Boiling a liquid and separating it into portions or *fractions* by means of their difference in boiling points.

**Gelatinous.** Jelly-like or starch-like paste; applied to precipitates.

**Germicide.** A substance destructive of germs.

**Gravimetric.** Applied to determining the proportion by *weight.*

**Halogens.** Literally, salt producers; the chlorine family.

**Hydrated.** Containing water.

**Hydroxyl.** The group HO, found in all hydroxides.

**Hygroscopic.** Having the property of becoming moist in damp air.

**Indicator.** A substance, like litmus paper, used to determine when a reaction has been completed.

**Ion.** An electrically charged atom or group of atoms. They may be either positive, called *cations;* or negative, called *anions.*

**Isomeric.** Two compounds are *isomeric* when they have the same percentage composition, the same empirical formula, but are entirely different in properties.

**Monad.** An element with a valence of one.

**Monobasic.** Applied to an acid having only one displaceable atom of hydrogen in a molecule, as hydrochloric acid.

**Mordant.** Something used to set the color or dye in cloth.

**Nascent.** Literally, *being set free;* applied to a gas as it is being set free from some compound; in the atomic form and very active, chemically.

**Neutral.** Neither acid nor alkaline in character.

**Neutralization.** The process of combining an acid and a base so as to exactly destroy the properties of each and form a new compound.

**Nitrogenous.** Containing nitrogen.

**Occlude.** To condense within the pores of a metal; as hydrogen in platinum or carbon monoxide in hot cast iron.

**Oxidation.** The combining of a substance with oxygen. In a broader sense, raising the valence of an element.

**Oxidizing Agent.** A substance which will bring about oxidation. Usually a substance containing oxygen, with which it will part readily. Often chlorine or bromine.

**Paste.** A very pure form of flint glass used in making imitation diamonds.

**Pneumatic.** Term applied to the trough used in collecting gases.

**Polymer.** A term applied to one compound the multiple of another. Thus, $C_6H_6$ is a polymer of $C_2H_2$.

**Precipitate.** A solid thrown out in a solution; it may be a mere cloud or so very dense and heavy as to settle very rapidly.

**Radical.** A group of atoms which act chemically as if a single element.

**Reaction.** The chemical change taking place between two or more substances.

**Reagent.** A substance used in a chemical reaction.

**Roast.** To heat strongly in presence of air; hence to oxidize.

**Saturated.** Fully satisfied. Containing all possible.

**Slag.** A nearly black glass formed in blast furnaces in the reduction of iron and other metals.

**Sublimate.** The substance obtained by sublimation.

**Sublimation.** The process of vaporizing a solid which boils without melting, and collecting the vapors.

**Supernatant.** Overlying. Said of a liquid above a precipitate which has settled.

**Ternary.** Composed of three elements or more.

**Upward Displacement.** Method of collecting light gases by letting them flow *upward* into a bottle of air, *displacing* the air.

**Volatile.** A term applied to substances which readily change into gas.

**Volumetric.** Estimation of quantity by measuring the volume, not weight.

## Common or Commercial Names

**Agate.** A species of quartz, often beautifully colored in concentric rings.

**Alabaster.** A beautiful white or delicately tinted form of gypsum.

**Alum.** A double sulphate, containing a univalent and a trivalent metal. Common alum is potassium aluminum sulphate.

**Alumina.** Aluminum oxide.

**Amethyst.** A variety of quartz, pale violet in color.

**Antichlor.** A substance employed to neutralize the chlorine used in bleaching. It is generally sodium thiosulphate.

**Arsenic.** The usual commercial name for arsenic trioxide.

**Arsenous Acid.** A term often applied to arsenic trioxide. Strictly speaking arsenous acid is $H_3AsO_3$.

**Arsine.** Hydrogen arsenide also called arseniuretted hydrogen, $H_3As$.

**Baryta.** Barium oxide, BaO.

**Baryta Water.** Barium hydroxide, $Ba(HO)_2$.

**Bauxite.** Hydrated aluminum oxide, $Al_2O_3:H_2O$.

**Benzene.** More properly called benzol, $C_6H_6$, obtained from coal tar.

**Benzine.** A light oil resembling ordinary gasoline, obtained from petroleum.

**Bicarbonate of Soda.** Cooking soda, $NaHCO_3$.

**Bituminous.** Containing bitumen or oil.

**Blanc de fard.** Bismuth oxynitrate, $BiONO_3$.

**Blue Vitriol.** Copper sulphate crystals.

**Borax.** Sodium tetraborate.

**Butter of Antimony.** Antimony chloride, so called from its yellow color.

**Calcite.** Crystallized calcium carbonate, being three in scale of hardness.

**Calomel.** Mercurous chloride, $Hg_2Cl_2$.

**Carborundum.** Silicon carbide, SiC,used as an abrasive.

**Caustic Potash.** Potassium hydroxide.

**Caustic Soda.** Sodium hydroxide.

**Chalcedony.** A variety of quartz.

**Chalk.** A soft, natural form of calcium carbonate.

**Chloride of Lime.** Commercial name for bleaching powder.

**Chrome Alum.** A double sulphate of potassium and chromium.

**Chrome Yellow.** Lead chromate, $PbCrO_4$.

**Copperas.** Ferrous sulphate, green vitriol.

**Corrosive Sublimate.** Mercuric chloride, $HgCl_2$.

**Corundum.** Native, unerystallized aluminum oxide, nine in scale of hardness.

**Emerald.** Aluminum oxide, crystallized, green in color.

**Emery.** An impure, native form of aluminum oxide.

**Epsom Salts.** Crystallized magnesium sulphate.

**Felspar.** A complicated silicate rock, which, decomposed, forms clay.

**Fool's Gold.** Iron pyrites, $FeS_2$.

**Fuller's Earth.** A white variety of clay.

**Green Vitriol.** Ferrous sulphate.

**Gypsum.** Native calcium sulphate, $CaSO_4{:}2H_2O$.

**Hartshorn.** An old name for ammonia, so called because made from the horns of deer.

**Hypo.** Sodium thiosulphate, used in photography as fixing bath and as an antichlor.

**Iceland Spar.** A transparent, crystallized variety of calcium carbonate.

**Jeweler's Rouge.** Ferric oxide, native, used in polishing and as a paint.

**Kelp.** A variety of seaweed. Also applied to the ashes derived by burning the seaweed.

**Labarraque's Solution.** Sodium hypochlorite, NaClO.

**Lac Sulphuris.** A fine white precipitate of sulphur in limewater.

**Laughing Gas.** Nitrous oxide $N_2O$.

**Lime.** Calcium oxide.

**Limestone.** Native calcium carbonate, unerystallized.

**Limewater.** Calcium hydroxide solution.

**Lunar Caustic.** Silver nitrate in stick form containing small percentage of silver chloride.

**Magnesia.** Magnesium oxide.

**Marble.** Crystallized limestone.

**Milk of Lime.** Calcium hydroxide solution containing lime in suspension.

**Minium.** Red Lead, $Pb_3O_4$.

**Naphtha.** A low boiling gasoline obtained from petroleum.

**Nitre.** Potassium nitrate.

**Nordhausen's Acid.** Fuming sulphuric, $H_2S_2O_7$.

**Oil of Vitriol.** Sulphuric acid.

**Opal.** A variety of silica.

**Paris Green.** Copper aceto-arsenite.

**Pearl Ash.** Pure potassium carbonate.

**Plaster of Paris.** Monohydrated calcium sulphate, $CaSO_4:H_2O$.

**Plastic Sulphur.** Amorphous sulphur, prepared by pouring boiling sulphur into cold water.

**Potash.** Commercial potassium carbonate.

**Powder of Algaroth.** Impure antimony oxychloride.

**Purple of Cassius.** A purplish colored compound obtained by adding to a solution of gold chloride a small amount of stannous and stannic chloride.

**Pyrites.** Usually means iron pyrites, $FeS_2$. There is also a copper pyrites.

**Quicklime.** Lime.

**Red Precipitate.** Mercuric Oxide.

**Sal Ammoniac.** Ammonium chloride.

**Sal Soda.** Crystallized sodium carbonate.

**Salt Cake.** Sodium sulphate as obtained in the Leblanc process of making sal soda.

**Saltpeter.** Potassium nitrate.

**Scheele's Green.** Acid copper arsenite, $CuHAsO_3$.

**Silica.** Silicon dioxide.

**Slaked Lime.** Calcium hydroxide, formed by adding water to lime.

**Smoky Quartz.** A variety of quartz; silica, brown in color, sometimes almost black.

**Soda.** Usually cooking soda is meant. Sodium bicarbonate, $NaHCO_3$.

**Subnitrate Bismuth.** Bismuth oxynitrate, often sold as "bismuth." $BiONO_3$.

**Sugar of Lead.** Lead acetate, $Pb(C_2H_3O_2)_2:3H_2O$.

**Vermilion.** Artificial mercuric sulphide.

**White Arsenic.** Arsenic trioxide.

**White Lead.** Basic lead carbonate; a common white pigment.

**White Vitriol.** Crystallized zinc sulphate. $ZnSO_4:7H_2O$.

**Zinc White.** Zinc oxide, ZnO. A common white pigment.

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